

THE TECHNOLOGY OF WOOD DISTILLATION

THE TECHNOLOGY OF WOOD DISTILLATION

WITH SPECIAL REFERENCE TO THE METHODS OF OBTAINING
THE INTERMEDIATE AND FINISHED PRODUCTS FROM THE
PRIMARY DISTILLATE

BY

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WITH AN ADDITIONAL CHAPTER BY THE TRANSLATOR

AUTHOR'S PREFACE (ABRIDGED)

TO THE SECOND GERMAN EDITION

THE first edition of "The Technology of Wood Distillation," which appeared in 1903, was exhausted in 1907, and the preparation of a second edition became necessary.

• In the meantime striking progress had been made by the industry, both in the process of carbonisation and in the methods of working up the volatile products. Accordingly I recognised that not only was a complete revision of my book required, but that the field which it covered must be considerably widened.

In the first edition I had restricted myself essentially to the presentation of a series of monographs on the methods of manufacture then in use, without, as a rule, entering into details regarding the laws on which the various methods were based. At the same time, I expressed the opinion that these methods were capable of improvement; and in this direction the industry, during the period 1903-1909, made great advances.

Towards this development I can claim to have made considerable contribution; for example, in having introduced the process of tar separation (German patent 189,303), the utilisation of waste heat from wood distillation plant for the distillation of pyroligneous acid, and the concentration of acetate liquor (German patent 193,382), the continuous production of concentrated crude naphtha from dilute solutions, the mechanical drying of acetate of lime direct from solution, the acetone process (German patent 134,977), and the formaldehyde process (German patent 106,495).

In connection with all the above improvements I kept my

attention fixed on the possibility of greater heat economy, since it was particularly in this direction that the prevailing methods of manufacture left much to be desired. The results obtained in practice from the factories which adopted the newly introduced processes have shown me that this course was the right one to follow.

The work of building and reconstructing a large number of wood-distillation factories in the course of my service with Messrs. F. H. Meyer, Hannover-Hainholz, has afforded me many opportunities to add to my experience; further, my visits to the principal districts, both in Europe and Overseas, where wood-distillation is carried on, as well as the inspection of the most important factories in the different countries, have enabled me to view the industry and its branches in all their various aspects. As a result of the particular nature of my work I have naturally collected a large amount of information, the use of which has been kindly permitted by my firm, Messrs. F. H. Meyer.

As regards publications which have appeared in the meantime, I may mention a series of very interesting papers in the "Jerne Kontorets Annaler"—the journal of the Swedish wood-distillation syndicate—dealing in detail with the Swedish wood-distillation industry itself, and also with the phenomena observable during the processes of carbonisation and recovery of the by-products. In making use of this information in various parts of my book I have indicated its source.

A paper by Wislicenus and Büttner¹ contains much interesting matter on methods of analysis; various publications by Juon² deal in a very thorough manner with the composition of wood-gas, also the nature of charcoal and its analysis. The investigations of Klason, Heidenstamm and Norlin³ are likely to prove of classic importance in explaining the various reactions which accompany the carbonisation of wood. I regret that I have only been able to refer very briefly to this

¹ Journal für praktische Chemie, 1909, **79**, 177.

² Stahl und Eisen, 1907, 733, 771.

³ Zeitschrift für angewandte Chemie, 1909, : 25, 1205.

work, owing to the fact that when it appeared my book was already partially in print. . . .

As indicated above, I have carried out the revision of the book in the light of actual practical experience. Further, I have dealt with the chemical and physical principles which form the basis of the various operations involved in the carbonisation of the wood, the treatment of the volatile distillation products and the final manufacture of the usual commercial products, and which govern the design of the plant and machinery used for performing these operations.

As a result, I believe that the present edition possesses more the character of a text-book, and will therefore serve even better than the first edition to assist those engaged either technically or commercially in the industry, as well as industrialists generally who wish to interest themselves in the subject.

Apart from the various changes which the book has undergone, a considerable amount of new matter has been added ; for example, on the drying of wood, the various methods of separating tar from pyroligneous acid, the new processes of acetone manufacture, and a monograph on the manufacture of formaldehyde.¹ The treatment of wood in producers is also dealt with in detail, and the analytical section of the book has been considerably extended.

I trust that the second edition of my " Technology of Wood Distillation " will meet with the same friendly reception as was accorded to the first edition.

M. KLAR.

HANNOVER,

November, 1909.

¹ The monograph on Formaldehyde by J. E. Orloff appeared while the present edition of this book was being printed. See page 368.

AUTHOR'S PREFACE

TO THE REPRINT OF THE SECOND EDITION

THE second edition of this book was already exhausted at the beginning of the Great War. Unfortunately, the author was not able to meet the wishes of the publisher with respect to the immediate preparation of a new edition, since the many duties which devolved upon the managers of industrial enterprises during, and particularly after, the war, left the author no leisure time in which to undertake literary work.

Moreover, during the war the methods of operation in the German wood distillation industry did not undergo such changes as to render a revision of the book essential.

Since it has been impossible up to the present to obtain authentic information as to the development of methods of operation in other countries, the publisher and author have agreed to meet the situation by preparing a simple reprint of the second edition.

M. KLAR.

HOLZMINDEN,
October, 1920.

TRANSLATOR'S PREFACE

WHEN the second edition of Klar's "Technology of Wood Distillation" appeared in 1910, it was generally recognised that, as regards the author's treatment of the subject and the information afforded, the work was much in advance of any previous publication in this field.

The author, in his preface to the reprint of the book, mentions that up to 1920, the industry in Germany had scarcely undergone sufficient change to render a new edition necessary. This statement may be said to apply to European practice generally, at any rate as far as the distillation of hardwood is concerned.

References to Klar's work are constantly to be found in publications dealing with the distillation of wood, and considerable use of the information contained in the book has been made by other writers. Accordingly it is hoped that the present translation, apart from whatever practical value it possesses, will fill a gap in the literature on the subject available to English readers.

In the main the original text has been translated without alteration, but a certain amount of additional matter has been incorporated; for example, a description of the manufacture of "iron liquor," some information on the continuous mechanical retort as used in Great Britain, a description of the Ross and Corner retort and flow-sheets illustrating the manufacture of acetone and methyl alcohol. The official specifications for acetone and wood-naphtha have been revised where necessary, and certain more recent methods of analysis have been included in the analytical section. Cost data and values of products have been left unchanged and may be taken as applying to pre-war conditions in Germany.

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The last chapter of the book is only intended to represent a brief review of some of the more important recent work having a practical interest.

I wish to express my thanks to my friend, Mr. J. W. Black, B.Sc., for much assistance in reading the proofs; to Mr. S. C. Bone, Messrs. Wilson Brothers Bobbin Co., Ltd., for information on the manufacture of "iron liquor"; and to Mr. Philip Poore, for permission to publish the results of experimental work on his process.

ALEX. RULE.

HEIDELBERG,

May, 1925.

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LIST OF ABBREVIATIONS

- Ann. Chem. = Annalen der Chemie.
Ann. Chim. Phys. = Annales de Chimie et de Physik.
Ann. Phys. = Annalen der Physik.
Arkiv. Kem. Min. Geol. = Arkiv. för Kemi, Mineralogi och Geologi.
Ber. = Berichte der deutschen chemischen Gesellschaft.
Bull. Imp. Inst. = Bulletin of the Imperial Institute (London).
Bull. Soc. Chim. = Bulletin de la Société Chimique de France.
Chem. News = Chemical News.
Chem. Zeit. = Chemiker-Zeitung.
Chem. Zentr. = Chemisches Zentralblatt.
Compt. rend. = Comptes rendus de l'Académie des Sciences (Paris).
Dingl. polyt. Journ. = Dinglers polytechnisches Journal.
Inst. Sci. Ind. Bull. = Institute of Science and Industry Bulletin (Australia).
Jahresber. = Jahresbericht der Chemie.
Journ. Amer. Chem. Soc. = Journal of the American Chemical Society.
Journ. Chem. Soc. = Journal of the Chemical Society (London).
Journ. Ind. Eng. Chem. = Journal of Industrial and Engineering Chemistry.
Journ. Ind. Inst. Sci. = Journal of the Indian Institute of Science.
Journ. Pharm. Chim. = Journal de Pharmacie et de Chimie.
Journ. prakt. Chem. = Journal für praktische Chemie.
Journ. Russ. Phys. Chem. Soc. = Journal of the Russian Physical and Chemical Society.
Journ. Soc. Chem. Ind. = Journal of the Society of Chemical Industry.
Pharm. Journ. = The Pharmaceutical Journal.
Pharm. Zeit. = Pharmaceutische Zeitung.
Phil. Mag. = Philosophical Magazine.
Trans. Roy. Soc. Edin. = Transactions of the Royal Society of Edinburgh.
U.S. Dept. Agr. Bulletins = United States Department of Agriculture Bulletins.
Zeit. anal. Chem. = Zeitschrift für analytische Chemie.
Zeit. angew. Chem. = Zeitschrift für angewandte Chemie.
Zeit. Chem. Pharm. = Zeitschrift für Chemie und Pharmacie.

THE TECHNOLOGY OF WOOD DISTILLATION

CHAPTER I

SHORT OUTLINE OF THE HISTORY OF WOOD DISTILLATION¹

THE origin of the destructive distillation of wood can be traced back to remote antiquity, for it is certain that ancient races were acquainted not only with the production of charcoal, but also with methods of recovering distillation-products resulting from the process of carbonisation. Examples of such products are fluid wood-tar and pyroligneous acid, which were used by the Egyptians for embalming their dead, as recorded in the works of ancient writers. Pliny, for example, writes in his "*Historia Naturalis*, Lib. 11, de pice":

"Pix liquida in Europa ex teda coquitur navalibus, munientis multosque alios ad usus. Lignum ejus concisum furnis, undique igne extra circumdato fervet. Primus sudor aquæ modo fluit canali, hoc in Syria Cedrium vocatur, cui tanta vis est, ut in Ægypto corpora hominum defunctorum eo perfusa servantur."

It is also evident from the writings of Theophrastus² that the Macedonians practised charcoal-burning in pits for the purpose of obtaining tar.

In other parts of the ancient world wood was probably carbonised for the production of charcoal before civilisation appeared. At any rate, charcoal-burning is as old as the use

¹ Cf. articles by *Otto Vogel*, *Chem. Zeit.*, 1907, No. 82; 1908, Nos. 47 and 100.

² "*Histor. Plant.*," Vol. IX (Heinsius edition).

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of metals, and was carried on everywhere simultaneously with the operations of mining.

The process was originally worked in simple open-air pits. At a later stage these pits were replaced by the more efficient heaps or "meilers." All contrivances of this nature were designed merely for the production of charcoal which for a long period remained the sole object of the destructive distillation of wood. Efforts were made, however, to bring these simple processes up to the highest state of perfection, and at the end of the eighteenth century both metallurgists and chemists were busily engaged with that problem. At that period, literature dealing with the subject of wood-distillation, or rather of "charcoal-burning" as carried on at that time, was already in existence in several countries.

Numerous publications¹ show that at the end of the eighteenth century both the nature of the process of charcoal-burning and methods of utilising the by-products were well known.

A detailed abstract of the literature on the subjects of charcoal-burning and the production of tar will be found in the work written by von Berg,² which may be regarded as a classic of its period.

von Berg speaks of obtaining by-products (tar and pyroligneous acid) from the "meiler" process of charcoal-burning. It is obvious, however, that he was not yet acquainted with the distillation of wood in retorts or ovens without admission of air.

Hence, it may be said that up to the time of von Berg wood-distillation was carried on either for the production of charcoal alone or, when resinous coniferous wood was carbonised, for the production of tar and pine-oil in addition to the charcoal.

All these methods of carbonisation—some of which are of very ancient origin—have persisted in certain localities practically unchanged right up to the present day. They are

* The works of : Duhamel de Monceau (1761), Joh. Andreas Cramer (1766), Chr. Ernst Dornemann (1775), H. D. v. Zanthier (1792), C. T. Laurop (1802), G. L. Hartig (1807), C. F. F. v. Werneck (1808), C. J. B. Karsten (1821), C. D. Af Uhre (1820), S. H. Stoltze (1820), F. Freitag (1831), F. Klein (1836), A. Beschoren (1840), v. Berg (1828-1860), Ebelmen (1850), Scherer (1848-1853), Müller (1858); Wagner's "Jahresberichte" (1855 *et seq.*); publications by Reinhold Freiherr v. Reichenbach (1858), Völkel and Laurent (1840), Asmus (1867), etc.

² "Verkohlen des Holzes," 1860.

still used not only in very richly wooded countries such as Russia, Scandinavia and Hungary, but also in Germany, France and Italy, where charcoal-burning is still widely practised often in connection with a smelting-works. Again, however, the main object of these crude forest processes is usually the production of charcoal, the recovery of volatile distillation-products being quite subordinate.

Although methods of utilising wood-tar had been discovered at an earlier period, it was only in the nineteenth century that technical applications were found for the more highly volatile condensable and non-condensable distillation-products. In operating a process as crude as that of forest charcoal-burning in its various modifications it is only natural that very little attention was paid to the recovery of these volatile products, which in former days were absolutely worthless; the production of charcoal, so widely used in metallurgy and at one time looked upon as essential for the manufacture of iron, alone brought in a sufficient profit.

But, as chemistry progressed more and more on the lines of pure scientific research, the nature of those products of wood-distillation which had remained unnoticed hitherto gradually became known.

As long ago as 1658 Glauber identified the so-called *pyroligneous acid* with the acid contained in vinegar. This discovery was confirmed in 1800 by Fourcroy and Vauquelin, who also showed that pyroligneous acid was identical with the so-called *pyromucic acid*, obtained by the distillation of sugars and gums, which previously had been regarded as different.

Boyle in his "Sceptical Chemist" (1661) described the separation of a spirituous liquid from the volatile product of the distillation of wood. It was only in 1812, however, that this liquid was again examined by Taylor,¹ who found that it closely resembled ordinary alcohol. Collin (1819) pronounced this product to be acetone, Doebereiner looked upon it as ordinary alcohol, and Reichenbach considered it to be a mixture of the two. Finally Dumas and Peligot² (1835) confirmed Taylor's views on the nature of the liquid and isolated a product from the crude wood-spirit to which they gave the name *methyl alcohol*.

After Reichenbach (1835) by his distinguished researches

¹ Phil. Mag., 1822, 60, 315.

² Ann. Chim., 1835, 58 [2], 5.

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had ascertained the components of wood-tar, and Phillip Lebon and Pettenkofer had determined the composition of wood-gas; the products of wood-distillation began to attract greater attention.

Illuminating gas manufactured from wood was first used in England, but the credit of being the first to view this source of light, heat and power from a general scientific standpoint belongs to the Frenchman, Phillippe Lebon. In spite of his great talents, however, Lebon did not succeed in bringing about the adoption of his so-called "thermo-lamp." This was due partly to the lack of interest shown by the French public in his large scale experiments at Havre and Paris, and partly to the fact that the wood-gas manufactured by Lebon's process possessed only inferior illuminating power. Although Pettenkofer succeeded in removing this objection, wood-gas was unable to compete as an illuminant with the coal-gas introduced by the Englishman, William Murdoch, in 1792.

It is obvious, therefore, that up to the year 1800 wood was carbonised chiefly with the object of furnishing sources of heat and light. The recovery of chemical products was always a secondary consideration, though the manufacture of savoury vinegar from pyroligneous acid may be traced back to the beginning of the nineteenth century. At any rate, Lowitz (1793) and Jasmeyer (1824) were said to have been in possession of certain methods for purifying "wood-vinegar" (pyroligneous acid), which rendered it quite as palatable as any other kind of vinegar.

It is impossible to decide whether the credit of being the first to obtain pure acetic acid from pyroligneous acid belongs to Lowitz, Jasmeyer, Stoltze or Mollerat;¹ there is no doubt however that in Germany at that period the destructive distillation of wood for the manufacture of acetic acid was unprofitable.

The modern wood-distillation industry was gradually brought into existence only as a result of the never-ceasing progress made by chemical research. The hidden secrets of coal were disclosed in rapid succession, and simultaneously extensive markets were opened up for the products of wood-distillation.

It is true that the products of coal-distillation—coke,

¹ See also "Handbook of Chemistry," by L. Gmelin, Vol. VIII, p. 282,

illuminating gas, tar and tar-distillates—competed keenly and successfully with the corresponding wood-products; but for other wood-products, such as acetic acid, wood-naphtha and acetone, new and widely varying applications were found, simply as a result of the immense development of organic chemistry,—especially the chemistry of coal-tar and the industries to which it gave rise. Coke largely took the place of charcoal for blast-furnace operations; gun-cotton almost entirely superseded charcoal for military powder; and wood-tar distillates were replaced without hesitation by coal-, lignite- and petroleum-distillates. On the other hand, the unforeseen rise of the coal-tar colour industry and of the dye-works processes closely associated with it, the epoch-making successes of purely synthetic chemistry in the province of artificial drugs, the manufacture of celluloid and smokeless powder, and, more recently, of artificial indigo, all led to a large demand for acetic acid and its salts, as well as for derivatives such as acetone, ethyl acetate, amyl acetate, etc.

In 1870, chiefly as a result of the earlier investigations of Lowitz and the introduction of column-stills, chemically pure acetic acid was successfully produced from pyroligneous acid through the medium of the calcium salt, at a reasonable price and at all degrees of concentration. Owing to its high degree of purity, no objection could be raised against the use of this product even for edible purposes.

From the outset a market had been found for acetic acid in the textile-printing and cotton-dyeing industries, but for a long period there was no outlet for the wood-spirit discovered by Taylor in 1812. Attempts to use wood-spirit in place of spirits of wine failed owing to the fact that the product obtained at that time was very impure. From about 1850 to 1860 German trade in wood-spirit was confined to the export of that article to England and Holland, in which countries it was already used as a denaturant. In any case, the price demanded for this crude product permitted scarcely any application. Here, again, it was essentially the chemistry of the coal-tar colours which brought about a change in this unfavourable situation.

Great interest had been aroused by Perkins' epoch-making discovery of *Mauve* followed by Verguin's preparation of *Fuchsine*; but the public were not satisfied for very long with these two shades alone, and a strong demand arose for a

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reddish-violet dye. This demand was met in 1859 almost simultaneously by Frank at Lyons and Grüner at Glauchau, both of whom succeeded in obtaining a very bright reddish-violet by dissolving fuchsine in wood-spirit and oxidising the solution.

Shortly after the disclosure of this process, which at first had been kept secret, there was a keen enquiry for wood-spirit, and, owing to its scarcity, the price rose enormously; hence it is not surprising that in England at that time wood was carbonised solely for the production of wood-spirit. The wood-spirit used for the above purposes had practically nothing in common with the almost absolutely pure methyl alcohol sold commercially at the present day; it was a very impure product of about 80–82 per cent Tralles, containing acetone and tar-oils.

However, the interest in this article did not last very long, for after the phenylation of rosaniline had been successfully effected, an innumerable series of new and even more beautiful dyes was introduced and wood-spirit was no longer required.

About 1864 a sudden demand again arose for wood-spirit, and the reason may be traced to the discovery of *Iodine-* or *Night-green*. The price, which in the meantime had fallen very low, again rose rapidly, and although Iodine-green did not remain very long in favour owing to its inferior fastness, further progress was rapidly made along the same path. *Methyl-green*, free from iodine, and *Methyl-violet* appeared, both of which required wood-spirit for their preparation; and right up to the present day this product has remained an indispensable material for the preparation of a whole series of aniline colours. The wood-spirit used at the present time, however, is much purer than that employed in the earlier stages of the dye-industry when it was only required that the product should be "wood-spirit of 96 per cent Tralles, which did not give a blue colouration with water."

Of great importance to the wood-spirit industry was the fact that the German Excise Laws of 1888 and those of nearly all other countries, including more recently the United States, recognised wood-spirit—either alone or mixed with pyridine bases—as a denaturing agent. Already the requisite consumption of purer qualities of methyl alcohol was assured, but the wood-spirit manufacturers were now

in a position to supply a still purer product without increasing the price, since they were able to sell the first and last runnings from the fractionation process for denaturing purposes.

The history of *acetone* extends over a relatively short period. Although its occurrence in wood-spirit was recognised at the time of the discovery of the latter product, attempts to find a technical application failed, in spite of various suggestions, chiefly on account of its very high price.

It was only as a result of the rise of the celluloid industry and the manufacture of smokeless powder that the foundations were laid for the technical preparation of acetone.

Since about 1880 acetone has been manufactured on the industrial scale by the destructive distillation of acetate of lime.

We have seen that markets were gradually opened up during the nineteenth century for acetic acid, acetone and wood-spirit. For this reason more general importance became attached to the recovery of the volatile distillation products.

The charcoal "pits" were replaced by heaps or "meilers," which already permitted the recovery of a certain amount of pyroligneous acid and tar; the "meilers" were supplanted in turn by brickwork kilns.

Subsequently, the process was transferred from kilns to ovens and the system of what may be termed "movable arrangements" for carbonising the wood was abandoned. The introduction of ovens established the principle of stationary carbonising plant to which it was necessary to convey the wood. The Schwartz kiln introduced the principle of separating the wood undergoing carbonisation from the wood used as fuel, though the combustion products of the fuelwood—containing, of course, very little oxygen—still came into direct contact with the wood in the kiln.

Reichenbach designed the first oven in which the heat required for initiating and carrying out the process of carbonisation was transmitted through metal walls. Reichenbach's oven can be regarded, therefore, as the first apparatus in Germany, Austria-Hungary, and probably in Sweden, which carbonised wood in completely closed vessels without admission of air—that is, in retorts. •

In 1819, when the Reichenbach ovens were introduced, England and France had already advanced a step further. These countries had taken advantage, in the meantime, of the

progress made in the manufacture of illuminating gas and especially of the tests which had been carried out by Murdoch to determine the most suitable form and disposition of the distillation-vessels. In place of brickwork ovens, in which the heat was transmitted through metal walls, iron boxes were first employed, and later, horizontal and vertical iron cylinders in England and France respectively. This represented the beginning of the retort era which made further progress, especially in Germany, owing to the temporary rise of the wood-gas industry. Hessel retorts of 20 cu. metres capacity were in use in Germany in 1851, and in Russia in 1853; these retorts marked a great advance on the Kesner retort, which easily burned through and held only 3 cu. metres of wood. About 1850 Germany, England and Austria were using mainly horizontal retorts (1 metre diameter, 3 metres long) adopted from the coal-distillation process, but suitably increased in size. These countries developed that type of construction; France, on the other hand, became more and more inclined to the use of vertical retorts, which were made portable by Robiquet—a very considerable advance.

At this period (1850) the pyroligneous acid was mostly converted directly into *brown acetate of lime* (67 per cent calcium acetate) without recovery of the wood-spirit. A certain amount of crude pyroligneous acid was also distilled, the distillate neutralised with oxide of lead, and the solution worked up into acetate of lead.

In the course of the next twenty years (1850–1870) carbonising apparatus underwent little alteration, but the method of treating the crude pyroligneous acid was improved by the introduction of the so-called “three-vessel” system (see page 204), which made it possible to resolve the crude acid into tar, calcium acetate liquor and aqueous wood-spirit in one single operation.

In the course of this operation, the tar which remained dissolved in the pyroligneous acid was separated out before the acid was neutralised with milk of lime, and an essentially purer acetate of lime was obtained. This product is known as “*grey acetate of lime*” and contains about 80–83 per cent of calcium acetate.

In the meantime, an important advance had been made in the province of alcohol rectification, as a result of the introduction of “column stills” of various types.

The increased demand for purer qualities of wood-spirit led to the adoption of these column stills by the wood-distillation industry also. By employing these stills, it became possible in one or two operations to obtain wood-spirit, which was already pure enough for many purposes, from the 5-10 per cent aqueous solution furnished by the three-vessel system.

The period 1870-1900 was marked by a great development of wood-distillation in most civilised countries, especially America and Hungary where wood was very cheap. These countries exported the greater part of their important output of acetate of lime and wood-spirit to Germany, which was able to absorb large quantities of those products owing to the development of its aniline-dye industry.

The great demand in Germany for wood-distillation products, and the fact that the price of wood was constantly increasing while the price of the manufactured products remained low, led to the various efforts which were made during the period 1890-1900—and are still being made at the present day—to utilise waste materials, such as sawdust, residues from tannin-extract factories, etc., for carbonisation. Unfortunately, in spite of all these efforts and all the enormous sums which have been sacrificed, the results up to the present have rarely been successful. The reason lay, and still lies, not so much in *technical* imperfections as in commercial difficulties.

In Germany, the manufacture of wood-distillation products from this class of raw material has proved unremunerative. Moreover, the price of wood is so high, owing to its scarcity, that the situation is not favourable for the extensive development of wood-distillation in that country. Germany—the chief consumer of acetate of lime and wood-naphtha—is therefore obliged to import these products, and the United States and Hungary (favoured by the present tariff laws) are in a position to profit by this situation.

Hungary, as a rule, employs horizontal retorts (1 metre diameter, 3 metres long), similar to those used in Germany; also, kiln-ovens, of 50•cu. metres capacity, provided with vertical heating tubes. On the other hand, America, which always favours very large plant, and Sweden, have introduced new and serviceable forms of carbonising apparatus designed to hold large charges, such as ovens of 400 cu. metres capacity, and horizontal retorts of 25-30 cu. metres capacity

which are charged with cars containing the wood. These retorts represent the first carbonising apparatus of that size which allows discharging operations to be effected in a practicable manner immediately after the completion of the process, and therefore without cooling down.

In regard to methods of treating the distillates, however, the Americans have been backward until comparatively recently.

At the beginning of the twentieth century, efforts were being made along the whole line of the wood-distillation industry to improve methods of operation. The irresistible rise in the costs of raw material, fuel, labour, and management, rendered it very necessary to find means of working the process more economically.

As a first step, those carbonising systems which consisted of a large number of relatively small retorts were thrown out of operation. It has been proved that, with larger charges, equal or even superior yields can be obtained, and at the same time the capital cost and costs for fuel, wages and maintenance are less. A system of many small retorts naturally requires more supervision, more manual labour and more fuel.

North America, Sweden and Hungary have largely gone over to the use of retorts which are capable of carbonising large charges of wood in one operation.

The principle of the Reichenbach oven has again come into vogue, since the Bosnian ovens (capacity: 50 cu. metres of wood), the Swedish carbo-ovens (capacity: 400 cu. metres) and the Müller cell-ovens with artificial cooling (capacity: 50 cu. metres), are really only modifications of the Reichenbach oven.

The "American kilns" go back to the principle of the Schwartz kiln, but instead of being operated as separate units, a large number of kilns are combined to form one system which is provided with a central condensing plant, and the movement of the gaseous products is effected by artificial means.

All these designs entail more or less complete cooling of the ovens before the charcoal is withdrawn.

The horizontal large-capacity retorts (25-50 cu. metres), which were first used in America, allow the charge to be drawn immediately after the process is completed and thus permit a much more effectual utilisation of the plant as well as a

saving in fuel. These retorts may be regarded as the best of the modern types of carbonising apparatus.

The tendency gradually to abandon small carbonising apparatus and to return to that of larger capacity, thus conforming to the ideas of Reichenbach, Hessel and others, represents the first advance made by the industry in the twentieth century. In addition, greater attention has been paid to the possibilities of utilising the heat which is lost during the process of carbonisation.

The furnace gases leaving the retort fires have been employed to dry, or at least to preheat, the wood; and waste heat is used to preheat the non-condensable gases from the retort condensers before combustion. Any difficulties which might arise in regard to chimney draught, as a result of utilising the heat contained in the furnace gases, have been avoided by installing fans, steam injectors, etc., for the purpose of creating an artificial draught.

The design of the Gröndal retort demonstrates, theoretically, the manner in which it should be possible to utilise all these sources of heat and even to apply them to a completely continuous system of operation. Unfortunately, this system is too complicated to allow of introduction into practice.

The change-over to large carbonising apparatus also necessitates the use of special forms of furnace. Of interest in this connection is the introduction of "gas producers" into the wood-distillation industry, especially those types which are capable of converting cheap grades of wood into gaseous fuel, while permitting the recovery of a certain amount of acetate of lime and wood-naphtha.

Gas producers of this type—with recovery of by-products—are at work in some Hungarian and Russian factories.

New methods have also been discovered for the treatment and application of the primary distillation products—wood-gas and tarry acid-vapours. As mentioned above, it has become the practice to preheat the non-condensable gas before combustion, but a further advance has also been made. Experience has shown that this gas is more or less saturated with distillation products (acetic acid and wood-naphtha), according to the temperature at which it leaves the retort condensers, and that these products may be recovered by washing the gas intensively with water, in scrubbers of suitable dimensions.

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The non-condensable gas (for composition see page 53) is suitable not only for heating purposes but also for generating power, and it is not easy to decide which of these two possible forms of application is the more rational. If the use of the gas for power purposes becomes established, it will be due to the important progress which has been made in the construction of gas engines.

As far as the treatment of pyroligneous acid is concerned, practically no change took place from 1750 to 1900.

The crude acid, as it comes from the retorts, always contains a considerable amount of tar *in solution*. If the object of the process is to obtain 80 per cent acetate of lime as a final product, the dissolved tar must be eliminated by distilling the pyroligneous acid. So far, all attempts to remove the tar by mechanical methods, such as centrifuging, salting-out, etc., have failed. Only a second distillation of the acid is effective and this operation accounts for the main proportion of the total fuel consumed in a wood-distillation factory. The acetic acid industry, owing to the fact that it has now almost universally adopted the sulphuric acid process, can only make use of 80 per cent acetate of lime; for this reason nearly all wood-distillation factories at the present day are obliged to distil their crude pyroligneous acid by one method or another. This operation alone accounts for 50 per cent of the total fuel consumed in generating steam.

The patent tar-separator,¹ invented by the author and consisting of an apparatus which is inserted between the retort and condenser, renders the second distillation unnecessary, since it separates the whole of the tar from the pyroligneous acid while both are still in the form of vapour, and delivers the tar as liquid.

This apparatus, which has been employed in practice for several years with very successful results, renders the treatment of crude pyroligneous acid a much simpler process compared with the methods hitherto in use.

*Continuous rectification of wood-naphtha, and continuous mechanical drying of acetate of lime represent further important innovations.

The most striking features of a modern wood-distillation factory may be summarised as follows:—

The use of carbonising apparatus of large capacity charged

¹ German patent, 189,303; F. H. Meyer, Hanover-Hainholz.

and discharged as far as possible by mechanical means ; the use of producer gas for heating purposes ; recovery of acetate of lime and wood-naphtha from wood-gas producers ; pre-drying or preheating of the wood free of cost ; preheating of the non-condensable gas on the regenerative principle before combustion ; scrubbing the gas and using it for generating power ; recovery of pyroligneous acid, completely free from tar, directly from the process of carbonisation, thus rendering possible the manufacture of grey acetate of lime without a second distillation of the pyroligneous acid ; continuous rectification of crude wood-naphtha, with the production of pure methyl alcohol, in one operation ; drying of acetate of lime by a continuous mechanical process which starts with the acetate liquor.

CHAPTER II

THE RAW MATERIAL OF WOOD DISTILLATION

ALL parts of trees and shrubs, which in industry and everyday life are described as "wood," may serve as raw material for destructive distillation. This designation covers the main mass of the trunk, the branches and the roots.

The particular class of material which is of most importance for the wood-distillation industry is the so-called "*fuelwood*" or "*firewood*" which is obtained in the forest as the residue, after the timber, pitwood and wood for paper-making have been selected from the felled trees. It comprises *split billets*, *round billets*, *brushwood* and *stumps*.

More recently another class of waste material, consisting of the various forms of scrapwood obtained during the mechanical treatment of timber in sawmills, etc., has been utilised successfully for carbonisation.

In these mills large quantities of wastewood are frequently produced in the form of slabs and laths by the operation of the saws, as well as a certain amount of amorphous waste, such as sawdust, etc. The latter is unsuitable for carbonisation, but the waste slabs and laths form excellent and often very cheap raw material. In Sweden, huge quantities of this class of wastewood are carbonised, the sawdust being utilised at the same time as fuel.

The industry has not dealt solely with wood as a raw material, but has utilised other vegetable products, composed chiefly of cellulose and lignin, such as fruit-stones. Good yields of acetate of lime and wood-naphtha may be obtained by the destructive distillation of extracted palm-nut shells, coffee-husks and especially olive-stones or "*grignons*" which are produced in enormous quantities in Italy and Spain as residues from the process of crushing olives and extracting the oil. "*Grignons*" are carbonised on an industrial scale in Spain.

Apart from these less usual forms of raw material, only forest or sawmill waste is utilised for destructive distillation.

Practically every species of wood may be employed for carbonisation. The choice of any particular species—where choice is possible—depends on the particular objects of the process; in other words, whether the main products desired in addition to charcoal are wood-naphtha and acetic acid, or oil of turpentine and tar.

The main reasons for the differences which exist between the various species of wood may be traced to the anatomical structure of the cellular tissue, also to the varying composition both of that tissue and of the cell sap.

Wood is described as *hard* or *soft* according to the compactness of its cellular tissue, its specific gravity and the resistance it offers to mechanical treatment—that is, its strength; and, again, as *broad-leaved wood*, or *coniferous wood*, according to whether the original tree possesses broad leaves together with a predominating amount of extractive matter in the cellular tissue, or, needle-shaped leaves together with a predominating amount of resinous matter and ethereal oils in that tissue. Coniferous wood is also distinguished by the quite characteristic form of its cellular tissue.¹

Hardness of Wood.—Various well-known kinds of wood may be arranged in order of hardness as follows :—

Very hard . . .	Hawthorn.
Hard	Maple, hornbeam, wild-cherry.
Moderately hard . .	Oak, plum, robinia, elm.
Rather hard . . .	Beech, walnut, pear, apple, sweet chestnut.
Soft	Spruce, silver fir, Scotch pine, larch, alder, birch, horse-chestnut, ash.
Very soft	Lime, poplar, various species of willow.

The following tables, drawn up by Senff,² give the yields of distillation-products from various kinds of wood. These figures are derived from a series of comparative laboratory experiments and show that broad-leaved wood produces

¹ The terms "hardwood" and "softwood" as used in the succeeding chapters, refer to "broad-leaved" woods and "coniferous" woods respectively. Although this system of classification is not strictly accurate, as will be seen by referring to the following table of hardness, it is the one usually adopted by the wood-distillation industry. ² Ber. 1885, 18, 60.

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relatively high yields of acetic acid and methyl alcohol, coniferous wood produces a relatively higher yield of tar, while the yield of charcoal is of the same order for all varieties of wood.

YIELDS OF WOOD-DISTILLATION PRODUCTS (SENF)

a = slow carbonisation

b = rapid carbonisation

			Pyroligneous acid.		Acetic acid	Charcoal,		Non-condensable gas.		
			Total distillate.	Tar	Yield	Acid content	Yield		Yield.	Increase in weight.
1. HORNBEAM; sound trunkwood	a	52.40	4.75	47.65	13.50	6.43	25.37	6.09	22.23	
	b	48.52	5.55	42.97	12.18	5.23	20.47	10.03	31.01	
2. ALDER-BUCKTHORN; small trunkwood, peeled	a	52.79	7.58	45.21	13.38	6.05	26.50	5.09	20.71	
	b	45.38	5.15	40.23	11.16	4.49	22.53	6.85	32.09	
3. ALDER; sound peeled trunkwood	a	50.53	6.39	44.14	13.08	5.77	31.56	6.29	17.91	
	b	47.76	7.06	40.70	10.14	4.13	21.11	9.52	31.13	
4. BIRCH; sound trunkwood	a	51.05	5.46	45.59	12.36	5.03	29.24	1.29	19.71	
	b	42.98	3.24	39.74	11.16	4.43	21.46	7.37	35.56	
5. MOUNTAIN-ASH; sound trunkwood	a	51.54	7.43	44.11	12.60	5.56	27.84	4.62	20.62	
	b	46.40	6.41	39.99	10.41	4.16	20.20	8.72	33.40	
6. BEECH; sound trunkwood	a	51.65	5.85	45.80	11.37	5.21	26.69	4.61	21.66	
	b	44.35	4.90	39.45	9.78	3.86	21.90	8.45	33.75	
7. BEECH; sound branchwood	a	49.89	4.81	45.08	11.40	5.14	26.19	5.95	23.92	
	b	43.14	2.90	40.24	10.89	4.38	21.30	8.99	35.56	
8. ASPEN; sound trunkwood	a	47.44	6.90	40.54	12.57	5.10	25.47	—	27.09	
	b	46.36	6.91	39.45	11.04	4.36	21.33	—	32.31	
9. BEECH; blighted branchwood	a	51.31	3.56	47.75	10.08	4.81	23.23	7.56	25.46	
	b	47.32	5.99	41.33	8.88	3.67	20.98	—	31.70	
10. OAK; sound trunkwood	a	48.15	3.70	44.45	9.18	4.08	34.68	4.67	17.17	
	b	45.24	3.20	42.04	8.19	3.44	27.73	6.36	27.03	
11. COMMON SPRUCE; ¹ sound trunkwood	a	45.37	4.42	40.95	6.66	2.73	30.27	4.85	24.36	
	b	51.75	9.77	41.98	5.70	2.39	24.18	6.98	24.07	
12. COMMON LARCH; sound trunkwood	a	51.61	9.30	42.31	6.36	2.69	26.74	8.08	21.65	
	b	43.77	5.58	38.19	5.40	2.06	24.06	8.72	32.17	
13. COMMON SPRUCE; ¹ decaying trunkwood	a	46.92	5.93	40.99	5.61	2.30	34.30	4.82	18.78	
	b	46.35	6.20	40.15	4.44	1.78	24.24	9.63	29.41	
14. COMMON SPRUCE; sound branchwood	a	46.34	8.13	38.21	5.82	2.22	25.55	9.33	28.11	
	b	43.85	6.44	38.41	4.20	1.61	23.35	9.93	32.80	
15. COMMON SPRUCE; bark	a	40.53	6.99	33.54	3.34	1.12	30.24	—	29.23	
	b	37.80	5.36	32.44	2.64	0.86	31.59	—	30.61	

From these data and from the undermentioned characteristics of individual species, the value of the wood for carbonisation may be deduced at once.

¹ Not completely carbonised.

Thus, as a rule, all varieties of wood are equally suitable for the production of charcoal. Broad-leaved wood is carbonised mainly for the production of acetic acid and wood-naphtha; coniferous wood mainly for the production of oil of turpentine and tar.

The yields of acetic acid and methyl alcohol also depend on the relative proportions in which cellulose and lignin are present in the wood, since cellulose produces no methyl alcohol and lignin produces only a small amount of acetic acid.

Anatomy of Wood.—We shall now consider briefly the external characteristics of wood. On examining a transverse section of a trunk the following areas may be observed :—

In the centre is the *pith*, consisting of a rather loose cellular tissue which often shrinks as the tree becomes older, giving rise to hollow spaces. Surrounding the pith is the main mass of the *wood*, in a series of layers which are traversed radially by the *medullary rays*. The *wood* is formed as a result of the activity of the growing tissue or *cambium* which lies between the wood and an outer layer, the *bark*. Each year, the cambium performs the task of thickening the wood-substance, which is made up of tracheids, wood-vessels, wood-parenchyma and medullary rays. The formation of new wood is not effected in a regular manner by the cambium, for during the time when the sap is most abundant—namely, in the spring—the woody elements are wide, large and thin-walled, whereas in the autumn they are narrow, but thicker-walled.

This periodic growth is marked very clearly on the transverse section of the wood by the *annual rings*, which owe their origin to the sharp contrast in the nature of the spring and autumn wood. The width of the annual rings varies according to the age of the tree, the nature of the soil, etc.

If the annual rings are wide the wood is said to be “coarse-grained”; if the rings are narrow the wood is termed “fine-grained.” Coarse-grained wood possesses less strength than fine-grained wood. In addition to the annual rings, further differentiation of the woody substance may be recognised owing to the difference in the nature of the older and younger layers of wood. The older wood or *heartwood* is distinguished by its greater hardness and often darker colour—as, for example, in the resinous rootwood of the

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conifers—from the younger *sapwood*, which contains living cells and takes part in the conduction and storage of materials.

The transverse section is bounded externally by the layer ordinarily known as the *bark*, a tissue-complex which acts as a protective covering—the *periderm*—to the trunk, as the latter is increasing in thickness.

Between this layer and the ring of cambium is another sharply defined layer of tissue, namely, the *bast*, which consists of long flexible cells, and for which there are numerous and varied industrial applications.

The periderm is composed of *cork* and a growing tissue, the *phellogen*. New formations of cork, derived from the action of the phellogen, cut off the supply of water to those portions of tissue which lie externally, thus giving rise to the dried-up and often rugged masses which constitute the outer covering of the trunk.

The form exhibited by the outer layers of bark depends on the extent to which cork is developed. If development is weak, the trunk presents the smooth appearance characteristic of beech, hornbeam and silver fir; if very strong, an enormously thick layer of cork may result as in the cork oak.

Chemistry of Wood.—The fundamental chemical constituents of wood are *cellulose*, $C_6H_{10}O_5$, containing 44 per cent of carbon, and the so-called incrusting substance, which is richer in carbon and is termed *lignin*. The exact constitution of lignin is not known, but the substance is possibly made up of several carbon compounds.¹ A characteristic feature of lignin is the presence of several methoxy-groups. Other substances present in the various species of wood are albuminoids, starch, dextrin, sugar, tannic acid, colouring matter, resins, ethereal oils, mineral matter, water, etc. Although these components differ widely in composition, it is found that, as a rule, the elementary composition of wood exhibits little variation, owing to the fact that the main mass of the wood-substance consists of cellulose which as an individual compound always possesses the same composition.

The following figures, derived from results of numerous investigations, represent the average composition of wood :—

¹ Cf. Cross and Bevan, Journ. Soc. Dyers and Colourists, 1916, **32**, 135, *Klasön*, Ber. 1920, **53**, 1864; 1922, **55**, 448.

	Carbon	Hydro- gen	Oxygen + Nitrogen	Ash	Water
	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.
Wood ; free from ash and moisture	50	6.0	44.0	—	—
Wood ; containing ash, but free from moisture	50	6.0	43.0	1	—
Wood ; containing ash and air-dry	40	4.8	34.4	0.8	20

The *nitrogen-content* of wood seldom amounts to more than 0.5 per cent ; it is responsible for the occurrence of ammonia and other nitrogenous bases (amines) in the distillate.

Certain importance attaches to the *ash-content* of the wood since that of the charcoal varies accordingly, a fact which must be taken into consideration if the charcoal is intended for smelting purposes. The ash-content of the bark is particularly high, often considerably greater than one per cent. Hence, removal of the bark before carbonisation is sound practice, for, as a result, the process of carbonisation is facilitated and a better quality of charcoal is obtained.

The data furnished by different authors on the ash-content of wood exhibit very wide variation and a summary of the figures is practically worthless.

Fuel-value of Wood.—Since local conditions may render it necessary to use wood as fuel, it will be useful to ascertain its calorific value.

The heat of combustion of carbon=8080 kilo-calories per kilo. ; that of hydrogen=34,200 kilo-calories per kilo.

One kilo. of air-dry wood (see above) contains :—

	Kilos.
Carbon	0.400
Hydrogen	0.048
Oxygen	0.342
Ash	0.010
Water	0.200

In calculating the calorific value according to the Dulong formula it is necessary in the first place to deduct from the total hydrogen the amount equivalent to the oxygen present.

0.342 kilos. of oxygen correspond to $\frac{2 \times 0.342}{16} = 0.042$ kilos. of

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hydrogen ; hence, the amount of available hydrogen present = $0.048 - 0.042 = 0.006$ kilos. The heat of combustion is therefore made up as follows :—

	Kilo-calories.
Carbon	$0.40 \times 8080 = 3232.0$
Hydrogen	$0.006 \times 34,200 = 205.2$
	<hr/> 3437.2

Water formed during the combustion =

$$(0.042 + 0.006) \times 9 = 0.432 \text{ kilos.}$$

Water originally present in the wood = 0.200 „

Total = 0.632 „

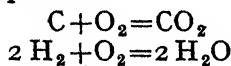
0.632 kilos. of water must be vaporised and the amount of heat required for this purpose— $0.632 \times 630 = 398.1$ kilo-calories—must be deducted from the above value for the heat of combustion.

Hence, the *theoretical* heating value of one kilo. of air-dry wood of the above composition = $3437.2 - 398.1 = 3039.1$ kilo-calories.

But this figure does not represent the *practical* heating value of the wood, since it is impossible in industrial furnaces to utilise completely the heat developed by combustion. Loss of heat takes place by radiation from the brickwork and from the hot ashes ; but the most serious loss is represented by the heat carried away in the flue gases. The quantity of flue gases produced, and the temperature at which these gases leave the furnace, vary considerably according to the height of the chimney and the atmospheric conditions—in other words, the chimney-draught—but above all according to the attention given to the firing by the stoker.

The quantity of air required for the combustion of 1 kilo. of wood of the above composition is calculated as follows :—

According to the equations :—



0.4 kilos. of carbon require $\frac{32 \times 0.4}{12} = 1.066$ kilos. of oxygen.

0.006 „ hydrogen „ $\frac{16 \times 0.006}{2} = 0.048$ „ „

Total = 1.114 kilos. of oxygen.

This weight of oxygen is equivalent to $\frac{100 \times 1.114}{23} = 4.843$ kilos.

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of air, containing 1.114 kilos. of oxygen and 3.729 kilos. of nitrogen.

On combustion, the above weights of carbon and hydrogen produce 1.466 kilos. of carbon dioxide and 0.054 kilos. of water vapour, respectively.

For industrial furnaces the calculated theoretical quantity of air is insufficient, about twice that quantity being required when solid fuels are used.

Hence, for 1 kilo. of wood of the above composition 9.686 kilos. of air must be supplied.

On combustion the following products are obtained :—

	Kilos.
Water vapour . . .	0.632
Carbon dioxide . . .	1.466
Oxygen (from excess of air) . . .	1.114
Nitrogen . . .	7.458

The respective amounts of heat lost in these gases may be calculated according to the following formula :—

$$L = w \times \text{Sp.Ht} (t_2 - t_1)$$

where w is the weight of the gas per kilo. of fuel, t_2 is the temperature of the flue gases and t_1 the temperature of the air supply. The sum of the values obtained in this way represents the principal loss of heat from an industrial furnace.

Assuming that the initial temperature of the wood and air was 15° C., and that the combustion products leave the furnace at 340° C. :—

		Kilo-calories.
Carbon dioxide = about 10 per cent by volume at 0° & 760 mm.	H ₂ O . . .	0.632 × (340 - 15) × 0.481 = 98.79
	CO ₂ . . .	1.466 × (340 - 15) × 0.217 = 103.38
	O . . .	1.114 × (340 - 15) × 0.218 = 78.92
	N . . .	7.458 × (340 - 15) × 0.244 = 591.41
		872.50
or, approximately 873 kilo-calories.		

It follows, therefore, that if 1 kilo. of wood of the above composition is burnt with twice the theoretical amount of air and the temperature of the escaping furnace gases exceeds the inlet temperature of the air by 325° C., the wood cannot develop more than

$$3039 - 873 = 2166 \text{ kilo-calories}$$

exclusive of radiation losses, or about 2000 kilo-calories,

including all losses. This amount of heat is capable of generating $\frac{2000}{536} = 3.73$ kilos. of steam, if the feed-water is preheated to 100° C.

The calculated *evaporative power* agrees approximately with the results obtained in practice.

Moisture-content of Wood.—Water forms a very important constituent of wood since, together with cellulose and lignin, it makes up the main mass of the wood. In consequence, it exercises very great influence, not only on the value of the wood, but also on the yields of charcoal and volatile distillation products, as well as on the total fuel requirements and general performance of a wood-distillation factory.

Hence, in judging the value of wood, particular attention must be paid to the moisture-content and the variations which it undergoes and which are followed necessarily by variations in the density, volume, and weight. *In other words a connection exists between density, moisture-content, volume and form, in the sense that any change in one factor is invariably accompanied by changes in all other factors.*

It is naturally impossible to draw up figures which will hold good generally for the moisture-content of freshly felled wood, since that value varies widely according to the season, the locality, and the species and age of the wood.

In spring and summer the amount of sap—and therefore the moisture-content—is greater than in winter. In spring, this condition is particularly marked, for during that season, as is well known, many trees such as birch exude the excess of sap without any external stimulus. The winter period is therefore the best time for felling wood intended either for fuel or for carbonisation.

On a rich fertile soil and under favourable climatic conditions, trees exhibit more luxuriant growth than trees grown under opposite conditions. Wood produced by the former possesses large annual rings and wide wood-vessels; it shrinks to a much greater extent when exposed to the heat of carbonisation and gives less and lighter charcoal than the wood produced by the latter class of tree, which possesses a heavier and denser structure and always produces charcoal of better quality.

Young wood is naturally richer in sap, and consequently less suitable for carbonisation than older wood; but the age

of the wood must not be too great. For example, when very old beechwood is carbonised the longitudinal fibres tend to separate sharply, with the result that the charcoal becomes fissured and produces more than the normal quantity of waste on transport and storage.

Finally, it must be emphasized that the sap-content differs for trunkwood, rootwood and branchwood, and that the moisture-content of heartwood and sapwood is also different.

The following table gives examples of moisture-content for different kinds of wood. Column 1 gives the average for a year, calculated from twelve monthly observations. Column 2 gives the extremes observed for each individual case :—

PERCENTAGE OF MOISTURE IN FRESHLY-CUT WOOD

Scotch pine	. 61	15-64	Sallow	42	30-49
Spruce	. 56	11-57	Beech	39	20-43
Lime	. 52	36-57	Maple	39	27-49
Black poplar	. 52	43-61	Hornbeam	37	22-41
Larch	. 50	17-60	Oak	35	22-39
Alder	. 50	33-58	Plum	34	19-39
Horse-chestnut	. 48	37-52	Elm	34	24-44
Birch	. 47	24-53	Robinia	29	12-38
Apple	. 43	34-52	Ash	27	14-34

Schübler and Hartig, on the other hand, found :—

	Percentage of moisture.		Percentage of moisture.
Hornbeam	. 18.6	Beech	. 39.7
Sallow	. 26.0	Alder	. 41.6
Maple	. 27.0	Aspen	. 43.7
Mountain ash	. 28.3	Elm	. 44.5
Ash	. 28.7	Red fir	. 45.2
Birch	. 30.8	Lime	. 47.1
Oak	. 34.7	Italian poplar	. 48.2
Silver fir	. 37.1	Larch	. 48.6
Horse-chestnut	. 38.2	White willow	. 50.6
Scotch pine	. 39.7	Black poplar	. 51.8

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Chevandier's investigations showed the following variations in moisture-content, expressed in percentage by weight :—

Kind of wood.	Months after felling.			
	6	12	18	24
TRUNKWOOD.				
Beech	23·24	19·34	17·40	17·74
Oak	29·63	23·75	20·74	19·16
Hornbeam	24·08	20·18	18·77	17·94
Birch	23·28	18·10	15·98	17·17
Silver fir	28·56	16·65	14·78	17·22
Spruce	29·31	28·54	15·81	17·76
STOUT BRANCHWOOD.				
Beech	33·48	24·00	19·80	20·32
Oak	31·20	26·90	24·55	21·09
Hornbeam	31·38	25·89	22·33	19·30
Birch	37·34	28·99	24·12	21·78
Silver fir	28·29	17·41	15·09	18·66
Spruce	35·30	17·59	15·72	17·39
SMALL BRANCHWOOD.				
Beech	30·44	23·46	18·60	19·95
Oak	32·71	26·74	23·35	20·28
Hornbeam	27·19	23·08	20·60	18·59
Birch	39·72	29·01	22·73	19·52
Silver fir	33·78	16·87	15·21	18·09
Spruce	41·49	18·67	15·63	17·42

The figures in these tables show that there can be no fixed standard for the moisture-content of freshly felled wood, but that after the wood has remained in store for a certain time—about twelve months after felling—the moisture-content of the different species becomes adjusted to a fairly constant figure—approximately 20 per cent.

Experience has shown that wood which is absolutely free from moisture gives inferior yields compared with wood containing 10–20 per cent of moisture.

In order to ensure that wood shall contain at the outset as little moisture as possible, it is advisable to fell it in the

winter period, when the sap is at its lowest. Figures obtained by Schübler support this statement :—

PERCENTAGE MOISTURE-CONTENT

	End of January.	Beginning of April.
Ash	28·8	38·6
Maple	33·6	40·3
Horse-chestnut . .	40·2	47·1
Silver fir	52·7	61·0

Winter-felled wood contains not only less moisture but also a lower amount of extractive matter (salts, organic compounds, etc.). Since these substances are undoubtedly hygroscopic in character, it follows that wood in which only relatively small amounts are present can be dried more easily. On the assumption that the mean moisture-content of freshly felled wood is 40 per cent, at least 50 per cent of the moisture must be evaporated in order to arrive at the normal moisture-content of air-dry wood—that is, approximately 20 per cent.

We shall see below, when we come to consider the preliminary treatment of wood intended for carbonisation, that there are two ways of achieving this object, namely :—

1. Natural drying in the air.
2. Artificial drying by the application of heat.

In connection with wood-distillation the former method, almost invariably, is the only one suitable. Artificial drying is far too expensive owing to the high capital cost of a drying installation and the cost of fuel and power.

In actual practice, the only rational method of reducing the moisture-content from 40 per cent to 20 per cent is to store the wood and leave it exposed to the air for 12–18 months.

Specific Gravity of Wood.—The specific gravity of the solid wood-substance itself is higher than 1·000, but wood usually floats on water owing to the air which is contained in the cell-tissue.

Figures representing the actual specific gravity have little value in practice ; on the other hand, figures which give the weight of a bulk-measure of wood—the form in which it is supplied by the wood-merchants—are of considerable value. The unit for the firewood trade in France, Belgium, Austria—

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Hungary, Germany and Sweden is the *stacked cubic metre* (*Raummeter* in German; *stère* in French)—that is, the mass of wood which can be packed into a marked-out space of 1 cu. metre.

In Russia the unit employed is the *cubic sashén* = 9.71 cu. metres.

England uses the *cord*, 14 feet long, 3 feet high and 3 feet wide = 3.568 cu. metres.

The American unit is likewise a *cord*, 8 feet long, 4 feet wide and 4 feet high = 3.624 cu. metres.

The *weight* of each of these units of bulk-measure varies very widely according to the manner in which the packing is carried out, and to the quality, species and dimensions of the wood. In any case the figure is not very important unless the moisture-content is also known, as otherwise it can give no clue to the probable yields of charcoal and volatile distillation-products. If the wood is air-dry, however, and consequently the moisture-content is known, then it is certainly possible to draw conclusions as to the value of the wood from the weight of the firewood unit (*sashén*, *cord*, etc.) since that weight is directly proportional to the mass of moisture-free wood present in the unit.

Unfortunately, the weight of the air-dry firewood unit is by no means constant, either for different species of wood or even for the same species. It is influenced by the relative dryness, form, length and thickness of the individual pieces; also by the degree of shrinkage, the locality, season, climate, the particular part of the tree from which the wood is derived, the moisture-content, the more or less careful manner in which the packing has been carried out and the errors arising from the practical methods of measurement which are never very accurate.

Statements of *yield*, which are based on the firewood unit but do not indicate the moisture-content and weight of that unit at the same time, possess very little value; this may also be said in regard to data on the *weights* of the firewood units for different species of wood, unless the moisture-content is indicated.

Yields always depend on the weight of absolutely dry wood contained in the *firewood-unit*, and on the relative amounts of cellulose, lignin, and—for coniferous woods—turpentine present.

The *volume* of solid wood in the firewood-unit is known as the *solid contents*.

The following figures, representing a combination of forest statistics and values obtained in practice, afford information which serves to a certain extent in calculating the solid contents of firewood-units (stacked cu. metres, sashéns, cords).

The *solid contents* of a stacked cubic metre of :—

	Solid cu. metre (approx.)
Split billets 1st class	= 0.614
„ „ 2nd „	= 0.60
Large round billets 200–250 mm. diameter	= 0.72
„ „ „ 150–200 „ „	= 0.70
Small round billets 100–150 „ „	= 0.614
„ „ „ 70–100 „ „	= 0.60
Root and stumpwood 40–80 „ „	= 0.5–0.42

These figures, however, can only be used for estimating *approximate* values, since they are dependent not only on the external dimensions of the unit, but also on the difference in diameter of the individual pieces and whether these pieces are straight or crooked, on the manner in which the wood is stacked, on the number of knots, the thickness of the bark, and the particular species of wood.

Weak wood contains not only a relatively small amount of solid matter, but also a large pith in proportion to the amount of wood-substance ; as a rule, therefore, it is unprofitable to utilise wood of this nature for carbonisation.

If the above figures are multiplied by the weight of a solid cu. metre of the wood—that is, a compact cube of wood 1 metre long, 1 metre wide, and 1 metre high—the result represents the weight of wood contained in a firewood-unit.

The specific gravity of any particular species of wood depends in the first place on the ratio of hollow space to solid substance in the cube. In regard to this value it is found that the annual rings are again of importance, wood with narrow annual rings always being relatively heavy. When the *wood-pores* are arranged in rings it is found that the annual rings have a greater influence on the gravity of the wood than is the case when the wood-pores are scattered.

These relations, however, must not be looked upon as representing fundamental principles, since they may be affected

very greatly by variations in the influence of locality, temperature, light, the amount of nutritive matter and moisture in the soil, etc. A damp soil almost always produces wood with wide rings and of indifferent quality; this holds good both for coniferous wood and for broad-leaved wood. Fertile soil, on the other hand, produces wood with wide rings, but of superior quality; this is particularly well marked in the case of beech and oak, whereas coniferous wood does not thrive so well under these conditions.

As mentioned above, portions of wood taken from different parts of the tree also exhibit differences in density. Branchwood is usually heavier than trunkwood; rootwood—with the exception of the neck of the root and the resinous rootwood of the conifers—is usually lighter than either of the foregoing, and the thinner the roots the lighter they are. Knotty excrescences, gnarled growth, healed wound-scars, knots, resin galls, etc., increase the density considerably. Provided that the annual rings are similar, dry heartwood is usually lighter than sapwood, as in beech and oak; the opposite may hold good however, as in Scotch pine; or the gravity may be the same for both, as in common spruce. Experiments carried out in various ways have shown that the density of the wood in different parts of a tree decreases as the relative height of the part decreases.

According to the investigations of Gayer, 1 solid cu. metre of the following species of wood, in the green and air-dry states respectively, weighs in kilograms:—

	Green.	Air-dry.
Oak	1040	760
Ash	880	750
Evergreen oak	1010	740
Beech	980	710
Hornbeam	1050	740
Elm	950	690
Sycamore	930	660
Birch	960	650
Larch	810	590
Austrian pine	970	510
Alder	830	540
Sallow	850	530
Scotch pine	820	520
Aspen	810	510

	Green.	Air-dry.
Speckled alder	800	490
Silver poplar	950	480
Silver fir	970	470
Common spruce	760	450
Lime	740	450
Weymouth pine	830	390

In order to determine the weight of moisture-free wood contained in a metric firewood-unit, the figure representing the *solid contents* of the latter is multiplied by the figure for the weight of a solid cu. metre of air-dry wood as given in Gayer's table. For example, let us assume that we require to determine the weight of moisture-free wood in 1 stacked cu. metre of air-dry, round beechwood billets. The average diameter of round billets is 90 mm., and according to the table on page 27, 1 stacked cu. metre contains 0.60 solid cu. metre. According to Gayer's table 1 solid cu. metre of air-dry beechwood weighs 710 kilos. Hence 1 stacked cu. metre of air-dry round beechwood billets of 90 mm. diameter will weigh $0.60 \times 710 = 426$ kilos. With a moisture-content of 20 per cent, 1 stacked cu. metre of this material must contain

$$\frac{80 \times 426}{100} = 340.8 \text{ kilos. of moisture-free wood.}$$

The table on page 30 gives the weights, calculated from the two previous tables (pages 27, 28), of 1 stacked cu. metre of air-dry wood, and of the moisture-free wood (100 per cent) contained in 1 stacked cu. metre, respectively.

The yields obtained from the distillation process depend on the weight of moisture-free wood present in the bulk-unit, but this weight may vary very considerably, according to whether the unit is a "forest measure" or a "retort measure" (see below). It will be obvious, therefore, that yields which refer to the firewood-unit are not comparable unless more detailed information is available in regard to that unit.

For this reason, it is already becoming the custom to refer to the performance and returns of wood-distillation factories in terms of "dry tons"—1000 kilos of moisture-free wood—and it is now only a question of general agreement on this method of procedure. If this practice were universally adopted, the variation in the figures representing yields which is now so common would disappear. For example, the published

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yields of acetate of lime from 1 stacked cu. metre of beech-wood vary between 27 and 38 kilos. In the former case 1 cu. metre of air-dry beech might contain only 0.270 "dry tons"

KIND OF WOOD.	Air-dry split billets, 1st and 2nd class. 1 cbm. = 0.62 solid cbm. Moisture con- tent = 20 per cent.	Air-dry round billets 70-100 mm. diam. 1 cbm. = 0.60 solid cbm. Moisture con- tent = 20 per cent.	Air-dry root- wood or round billets 40-60 mm. diam. 1 cbm. = 0.42 solid cbm. Moisture con- tent = 20 per cent.			
	One stacked cubic meter					
	weighs	contains moisture- free wood	weighs	contains moisture- free wood	weighs	contains moisture- free wood
	Kilos.	Kilos.	Kilos.	Kilos.	Kilos.	Kilos.
Oak	471	376	456	364	319	265
Ash	465	372	450	360	315	252
Evergreen oak	459	368	444	355	311	249
Beech	440	352	426	340	298	239
Hornbeam	459	368	444	355	311	249
Elm	428	340	414	331	290	232
Sycamore	409	320	396	317	277	222
Birch	403	292	390	312	273	218
Larch	366	292	354	283	249	199
Austrian pine	316	252	306	245	214	171
Alder	335	268	324	259	227	182
Sallow	329	264	318	254	223	178
Scotch pine	322	256	312	250	218	174
Aspen	316	252	306	245	214	171
Speckled alder	304	244	294	235	206	165
Silver poplar	298	240	288	230	202	162
Silver fir	291	232	282	226	197	158
Common spruce	279	224	270	216	189	151
Lime	279	224	270	216	189	151
Weymouth pine	242	192	234	187	164	131

owing to the wood having been loosely packed, whereas in the latter case it might contain 0.380 "dry tons" owing to tighter packing. It is assumed, of course, that for both cases other conditions are the same.

Purchase, Transport and Stacking of Wood.¹—In purchasing wood it is of prime importance to know the weight of moisture-free wood, expressed as "dry-wood tons" in the firewood-unit. Other conditions being satisfactory, the best wood for carbonisation is that which contains the greatest number of "dry tons" at the lowest price per bulk-unit delivered at the factory.

Wood is purchased either in the standing tree or already cut. The system of purchasing the wood-harvest standing is considered by most of the large State-forest Departments to be unsound, since it not only renders the checking of the estimated value of the wood more difficult, but increases the possibility of fraud. In private forests, however, this mode of purchase is quite common, and as far as roots and stumps are concerned, it is practically always the custom. It will be obvious that a transaction of this kind, which depends purely on estimation, can only be entered into by a fully experienced woodman who is completely conversant with the methods of forest mensuration and also understands how to sort the crop to the best advantage. If there are no difficulties in that respect it may prove very profitable to purchase the wood standing, provided that the buyer can secure cheap labour. This is generally possible among a rural population, which, as a rule, is largely unemployed during the winter period.

In certain richly wooded regions such as North America and Canada, where forestry has not yet been particularly developed, whole forests are cut down solely to provide wood for distillation, and there is no question of selecting timber or replanting. Hundreds of wood-cutters (usually Finns or Swedes) are employed in the forests of Michigan and Canada on this work of devastation; they live in log-huts, which are pulled down as soon as one area is cleared and are rebuilt on another area.

In Sweden also, large stretches of woodland are felled, but the operations are carried out strictly according to the rules of forestry. The whole of the timber, as well as the wood suitable for the manufacture of paper, is carefully selected. The material employed for carbonisation consists chiefly of the residual waste (firewood, root-stumps, etc.) or the waste slabs and laths resulting from the conversion of the timber.

¹ For a detailed account of the various methods used in Europe for transporting wood, the reader is referred to "Schlich's Manual of Forestry," Vol. v. (London, Bradbury, Agnew and Co., 1908.)

As a general rule, wood-distillation concerns are not wood-owners and merchants, but leave the cutting and sorting to the private and government forest authorities. The wood is purchased in open auction, or contracts are made with the forest authorities for the supply, over a given period, of definite assortments of wood from the crop in hand.

The transport of the wood to the stacking grounds or to the loading stations situated alongside the woodroads is carried out in many different ways. Sometimes the wood is dragged by human or animal labour ; in other cases sledge-like contrivances are employed, both in summer and winter ; in hilly districts timber-slides may be constructed ; if a river is available the wood may be built up into rafts or simply floated loose ; finally, it may be advantageous to utilise forest tramways, wire cableways, etc. In building up the small stacks in the forest, the wood must be carefully and closely packed between lateral supports which are well driven into the ground and are of the right length. In order to compensate for subsequent decrease in the height of the stack owing to shrinkage, it is usual to add about 10-13 centimetres at the time of stacking. As a result of this addition to the normal height of the stack, and owing to the fact that the splitting of the larger billets (three-cleft wood) which must be carried out in the factory-yard gives rise to an increase in volume, a considerable difference is often found to exist between the " forest stacked cu. metre " and the " retort stacked cu. metre," so that the latter may be as much as 20 per cent lighter than the former. Hence, data which are based on these bulk-units may differ very widely.

Thin branchwood and brushwood are usually bound up into faggots, but are sometimes made up together into cords, etc. ; on the other hand, stouter round billets are practically always made up into measured stacks.

Faggots are 1 metre long and 1 metre in circumference, and are sold in lots of one hundred.

The root- and stumpwood, after having been reduced in size either by hand or by means of explosives, is also made up into stacks, and in this case particular care must be taken to build up the layers as regularly as possible. The dimensions chosen for a stack of this class of wood are : length 2 metres, height 1 metre, width 0.5 metre, as it is found that by adopting this form gaps and lack of compactness are most easily avoided.

It is also necessary in dealing with this class of wood to sort it thoroughly in order to prevent the stacking of decaying wood with the sound wood.

After the operations of stacking or cording in the forest have been completed, and the details of sale have been settled with the forest administration, the wood is removed from the loading stations to the factory-yard, where it is stored in large stacks so that it may become air-dry before it is required for the process. The wood is usually conveyed to the factory on wood-carts or wagons, but the larger factories often find it an advantage, especially when a definite stretch of woodland is being worked, to utilise forest tramways, wire cable-ways, ordinary railways or possibly water transport, the last-named bringing down the costs very considerably.

In carrying out the operation of stacking, the wood is again examined, and any stout, three-cleft billets are removed for splitting and trimming. It is particularly important to eliminate all decaying wood, since the latter produces inferior yields both of volatile distillation products and of charcoal; there is also the danger that during the period of storage, which extends over one to two years, the stock of wood will show a distinct tendency to decay owing to infection by the rotten portions.

On the whole, it is found that winter-felled wood in the form of split billets remains sound for several years without any further preparation, provided that the stacks are built up in such a manner that drying winds can penetrate between the layers of wood and the stacking ground is dry. Further details with regard to stacking are given on page 92.

Under normal conditions the stock of wood is practically secure against injury, but in certain circumstances danger of attack by beetles or rot may arise.

Diseases of wood, such as bark shake, red rot, white rot, green rot, wound rot and dry rot, for exact knowledge of which we are indebted to the distinguished researches of Hartig,¹ generally make their presence known by a blue colouration.

According to Hartig, the cells, under the influence of these diseases, become completely altered, with the formation of

¹ Lehrbuch der Baumkrankheiten, 1889 (Julius Springer, Berlin). See also English translation, "Text Book of the Diseases of Trees," Hartig, Somerville and Marshall Ward, 1894 (Macmillan and Co., London).

water, alcohol, ethereal oils, etc. Partial reabsorption of the encrusting substance takes place, leading to a reduction in the yield of methyl alcohol; partial extraction of cellulose also occurs, a gummy mass remaining behind; or the cell tissue may undergo complete destruction with the formation of hollow cavities.

Owing to the reduction in weight of the wood-substance, which is brought about by these changes, it is naturally impossible to obtain yields from diseased wood equal to those from normal healthy wood. A further objection to diseased wood is that it produces charcoal of low specific gravity, which tends to crumble and takes fire readily.

Hence, in order to avoid disappointing results, it is essential that only dry healthy wood, which gives bulk-measures containing the greatest possible dry weight, should be utilised for carbonisation.

Apart from the usual forms of forest produce serving for distillation, such as split billets and round billets, it is the practice in certain countries to carbonise the resinous root-stumps of various conifers, more especially old pine roots, or "stubs," chiefly for the purpose of obtaining softwood tar (Stockholm tar) and pine-oil. Experts prefer root-stumps which have remained in the ground for some years and are just beginning to show decay on the tops. These root-stumps are, of course, very cheap and, in Germany, seldom cost more than twopence-halfpenny to threepence per stacked cu. metre; in other countries such as Russia, Sweden, the United States, and Canada they are willingly given away, if the land is cleared in return.

As a general rule the cost of root-stumps still in the ground may be taken as *nil*; but the cost "at the factory" is a very different matter. The extraction of the stumps is very expensive and laborious, likewise the operations of breaking-up the stumps and splitting-out the heartwood, which must be carried out before carbonisation, since it is only the heartwood which is specially suitable for the production of tar and pine-oil.

The extraction of root-stumps, or "grubbing" as it is called, is usually performed by manual labour, but the use of machines for this purpose is becoming much more general, especially in America. One type of grubbing machine is shown in Fig. 1. It may be possible by using these

mechanical contrivances and by employing explosives for disintegrating particularly large stumps to bring down the costs to some extent, but the expenditure entailed by these operations, including the separation of the heartwood, is still considerable. Under conditions such as exist in Germany it should always be reckoned that a stacked cu. metre of root-stumps at the factory will cost from half a crown to three shillings, according to the expenses of removal and transport.

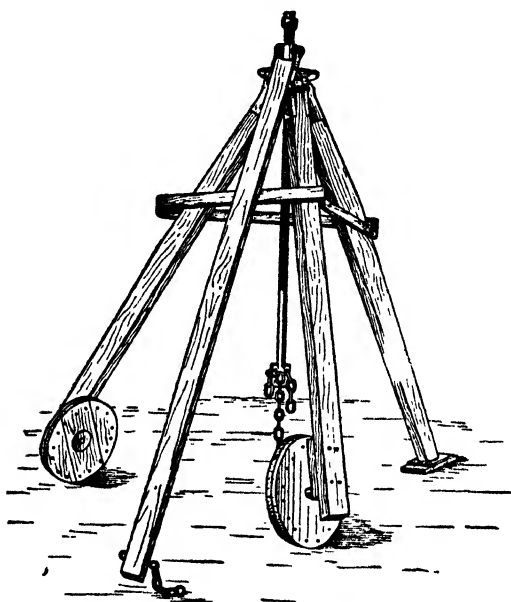


FIG. 1.—GRUBBING LEVER USED IN THE UNITED STATES.

In the forest, the root-stumps are usually only broken up into pieces of a size convenient for stacking in bulk-measures. Further disintegration of the wood is performed in the factory-yard itself, and for this purpose circular saws and splitting machines, consisting of steel wedges driven by eccentrics, are frequently employed.

Another form of raw material which must now be considered is the waste wood from the various operations of converting timber.

Most of the timber, after having been sorted out in the

forest is taken to the sawmills, where it is converted into the numerous different forms of sawn timber. The trunks are worked up systematically into rectangular shapes which vary greatly in size (scantlings, laths), or into planks, posts, boards, deals, veneers, etc. During these operations every portion of the wood which it is possible to convert into some commercial form of sawn timber is cut out. Of the residue from these operations—amounting to about 10 per cent—approximately one-half consists of waste slabs and laths and the other half of sawdust. None of this waste material has any value except as fuel and it is seldom worth the cost of transport. Owing to the large quantities which are produced in one small area, both the sawdust and scrapwood often become a serious nuisance.

A certain amount of the waste is used for firing the boilers of the sawmill; the remainder must usually be destroyed simply by burning it in the open. Both forms of waste may be used as raw material for the distillation process, but they are not of equal value. The only important difference in quality between waste scrapwood (slabs, laths, etc.) and split billets of the same species is the relatively high percentage of bark in the former. Sawdust, on the other hand, usually gives lower yields than the parent wood and produces a powdery charcoal for which only a very small market exists. Moreover, carbonisation of sawdust from coniferous wood does not result, like that of the parent wood, in the production of pine-oil, since the latter evaporates while the wood is being sawn, or afterwards while the sawdust is lying stored. The scrapwood from the sawmills forms a cheap and very suitable material for carbonisation, which up to the present has not received as much attention as it deserves. The possibility of utilising sawdust is a more difficult problem and is governed chiefly by local conditions.

Other materials belonging to the same category as sawdust are the residues obtained in the manufacture of tannin- and colour-extracts from certain kinds of wood, for example, extracted quebracho chips.

Another class of raw material is furnished by Nature in the form of rinds, seed-vessels and kernels of certain fruits. Examples of these materials, which consist mainly of cellulose or lignin, are the husks of coffee berries, nutshells and particularly the residues obtained in the production of olive oil.

The following yields per metric ton were obtained in practice by the author from these olive residues or "grignons":—

Charcoal (containing 9 per cent of ash)	. 354 kilos.
Wood-naphtha (100 per cent)	. . 12·6 „
Acetate of lime (80 per cent)	. . 43 „
Tar 40 „

The suitability of the "grignons" as a source of these products is proved by the above figures (see pp. 52, 178), and further evidence of their value in this respect is the fact that they are already carbonised on an industrial scale in Spain.

Nutshells and coffee husks also furnish satisfactory yields of distillation products and for this reason are distinctly suitable as raw material.

Systematic search will undoubtedly succeed in disclosing many other forms of raw material, and the author would take this opportunity of suggesting that rather more attention should be paid to the last-mentioned class than it has received up to the present.

The properties of the remaining raw materials required for the process of distillation or in working up the intermediate products—for example, quicklime, sulphuric acid and other chemicals—are already sufficiently well known; these materials are dealt with, as far as is necessary, in the analytical section (p. 381).

Correct choice of fuel and its utilisation to the best advantage are matters which affect industrial enterprises generally. Satisfactory textbooks dealing with this subject are available, and in this volume it is only necessary to enter into details concerning the use of wood and wood-gas as fuel.

CHAPTER III

THE CHEMICAL CHANGES OCCURRING IN WOOD DURING DESTRUCTIVE DISTILLATION

IN the previous chapters we have become acquainted with the wood-distillation industry in general as well as with the raw material and its properties. We have now to consider the changes which wood undergoes when heated in absence of air, that is, during destructive distillation. As already stated, hardwood consists principally of cellulose, lignin and water; hence practically the only chemical elements it contains are hydrogen, carbon and oxygen.

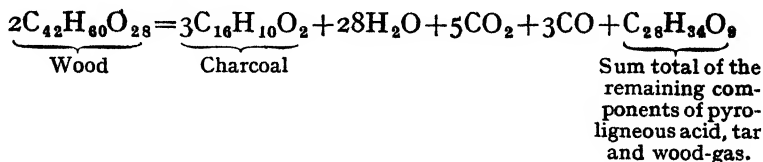
If wood is heated in a closed vessel provided with a vapour-outlet pipe, the water contained in the wood escapes first. As the heat increases, the wood begins to turn brown and the presence of acetic acid may already be detected in the aqueous distillate. The change of colour, the formation of acetic acid which was not present originally in the wood, and further, the simultaneous appearance of gaseous products, are obvious indications that the cellulose and lignin molecules are undergoing intensive decomposition as a result of the action of heat.

During this process the hydrogen and oxygen of the cellulose molecule combine partly with one another to form water, and partly with a portion of the carbon to form carbon compounds which may in turn enter into further combination or undergo decomposition. As a result, a large number of gaseous, liquid and solid products are formed by reactions of which the nature is still very obscure.

According to the investigations of Klason, Heidenstam and Norlin¹ the wood-distillation process, when carried to

¹ "Arkiv. Kem. Min. Geol.," 1908, 8 [10], 1.

completion at a maximum temperature of 400° C., is expressed by the following equation :—



This reaction proceeds exothermically, and the heat of reaction amounts to about 6 per cent of the heat of combustion of the wood.

During this reaction, *cellulose* produces acetic acid but no methyl alcohol, whereas *lignin*, that is, the encrusting substance, produces both methyl alcohol and acetic acid. The yields of these products are therefore largely dependent on the relative proportions in which cellulose and lignin are present in the wood.

A further insight into this very complicated process is afforded by the work of Edward Juon,¹ who examined the gases given off during the carbonisation of wood in kilns of the Schwartz type (Fig. 6). In accordance with the results of this investigation, Juon resolved the process into six phases.

These results, which refer to the carbonisation of coniferous wood, are summarised in the following table (p. 40).

This system of tabulation shows that up to a temperature of 280° C. practically nothing but water vapour, accompanied by an evolution of gas mainly composed of oxides of carbon, is given off by the wood. As soon as the temperature in the carbonising apparatus exceeds 280° C., the nature of the gas changes completely. Oxygen compounds decrease in quantity, and are replaced by hydrocarbons and hydrogen. Above 380° C. the amount of aqueous distillate diminishes, the gases become drier, the tar increases in quantity and becomes much more viscous. Up to a temperature of about 280° C. it is necessary to heat the apparatus, but from that temperature onwards carbonisation proceeds almost without any supply of heat; in other words, an exothermic reaction sets in, as Klason² and also Wislicenus and Büttner³ clearly demonstrated. The evolution of hydrocarbons increases up to a

¹ Stahl und Eisen, 1907, **27**, 733, 771; Journ. Soc. Chem. Ind., 1907, **28**, 677.

² Loc. cit.

³ Journ. prakt. Chem., 1909, **79**, 177.

Stage of Carbonisation.	1. At the begin- ning of the operation (water driven off).	2. First period of gas-evolution (gases contain- ing oxygen).	3. Evolution of hydrocarbons begins.	4. C _n H _m gases.	5. Dissociation period.	6. Hydrogen period.
Temperature in carbon- ising apparatus (° C.)	150-200	200-280	280-380	380-500	500-700	700-900
Percentage of carbon in the charcoal	60	68	78	84	89	91
Composition of non- condensable gas	68	66.5	35.5	31.5	12.2	0.4
	30.5	30	20.5	12.3	24.5	9.6
Hydrogen	0.0	0.2	5.5	7.5	42.7	80.7
Hydrocarbons	2	3.3	36.5	48.7	20.4	8.7
Caloric value of 1 cu. metre of gas, in kilo- calories	1100	1210	3920	4780	3630	3160
Condensable constituents of the gas	Water vapour	Water vapour and acetic acid	Acetic acid, wood naphtha, light tar	Large quantities of viscous tar	Large quantities of tar mixed with paraffin	Scanty condensate
Quantity of gas	Very small	Moderate	Considerable		Scanty	Very small

temperature of 500° C. If the process is carried to completion at still higher temperatures—as, for example, in the “meilers”—a change again takes place in the composition of the gas, hydrogen gradually increasing in quantity at the expense of the hydrocarbons.

When wood is carbonised in ovens or retorts—and only that method of operation will be described in this book—the process as a rule, is finished, at a temperature of 380–400° C. Hence, the hydrogen period does not appear, but the hydrocarbon period is well marked.

If carbonisation is stopped at 380°–400°, by cutting off the heat-supply, and the apparatus is then closed-up so that neither entry nor escape of gas can take place (vapours are no longer present at this period), further evolution of hydrocarbons may be observed; on the other hand, hydrogen and gaseous oxygen compounds gradually disappear. These conditions are realised in all forms of apparatus in which the charcoal is allowed to remain until it is quite cold. As soon as the apparatus is closed for the purpose of starting the cooling period, the internal pressure increases and the gaseous atmosphere surrounding the charcoal is found to contain about 80–90 per cent of hydrocarbons.

The pressure gradually diminishes, however, for, according to Juon, the hydrocarbons are energetically *adsorbed* by the charcoal, in which they condense to form complex and less volatile compounds. Juon has shown that as a result the carbon-content of the charcoal is increased by at least 5–6 per cent.

At any rate, when charcoal was manufactured in kilns of the Schwartz type (see Fig. 6, page 136) and the operation of cooling was carried out under two different sets of conditions, namely, (1) only closing the chimney after evolution of gas had ceased, (2) closing the chimney shortly after the further evolution of hydrocarbons had set in, it was found that the charcoal produced under the former conditions always contained distinctly less carbon (5–6 per cent) than charcoal produced under the latter conditions.

Juon proved, by three separate experiments, that it was possible to increase the carbon-content of charcoal, *without raising the temperature of carbonisation*, by hermetically sealing the apparatus when a temperature of about 380° C. had been reached, thus permitting the hydrocarbons already

present in the apparatus and those still being evolved by the charcoal to be adsorbed and condensed.

From what has already been stated, it will be obvious that the maintenance of definite temperatures—in other words, the manner in which the carbonising apparatus is heated—has a marked influence on the course of the process and on the yields of products; hence, by controlling the temperature it is possible, to a certain extent, to influence the yields in one direction or another. High furnace-temperature and, as a consequence, rapid operation, always give rise to much gas and comparatively small yields of acetic acid, wood-naphtha and charcoal, whereas slow carbonisation and a lower temperature result in the production of comparatively little gas, and larger amounts of acetic acid, wood-naphtha and charcoal.

At the time when wood-gas manufactured by Pettenkofer's process was still an important product, rapid operation was customary; *but when the object of destructive distillation of wood is the production of acetic acid and wood-naphtha, carbonisation must be carried out slowly and at a moderate temperature.*

Violette¹ investigated the influence of temperature on the quantity and quality of wood distillates; his figures, which are set out in the following tables, demonstrate very clearly the important part played by temperature in the carbonisation of wood.

These results also show that a temperature of about 400° C. should be sufficient for the carbonisation of wood; as a matter of fact, the maximum temperature of carbonisation in actual practice does not exceed 400° C.

Violette, in carrying out his experiments, was able to ensure uniform heating of the wood charge at all points in the carbonising apparatus. This is impossible, however, on a practical scale, because in large apparatus the distance of individual portions of the charge from the hot metal shell, or from any source of heat at all, varies too much to allow of perfectly uniform heating throughout. When an externally heated carbonising apparatus of small diameter is employed, the heat radiated from the hot metal shell is sufficient to start the distillation of the wood. In these conditions, the course of the process and the rate of flow of the distillate are very regular. If the diameter of the carbonising apparatus is large

¹ Ann. Chim., 1851, 33 [iii] 304.

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—as in the American and Swedish ovens—considerable differences of temperature exist in the different horizontal zones of

RESULTS OF HEATING WOOD IN CLOSED VESSELS AT VARIOUS TEMPERATURES (Violette).

No.	Loss of weight on drying at 150° C.	Temperature to which the wood was exposed	100 parts by weight of moisture-free wood evolved volatile matter.	100 parts by weight of moisture-free wood left as residue in the distillation vessel.
	Per cent.	°C.	Parts by weight.	Parts by weight.
1	15.00	160	2.00	98.00
2	17.17	170	5.45	94.55
3	14.04	180	11.41	88.59
4	14.36	190	18.01	81.99
5	17.28	200	22.90	77.10
6	15.40	210	26.86	73.14
7	15.80	220	32.50	67.50
8	12.73	230	44.63	55.37
9	15.58	240	49.21	50.79
10	13.16	250	51.33	49.57
11	14.76	260	58.77	40.23
12	12.91	270	62.86	37.14
13	14.94	280	63.84	36.16
14	14.43	290	65.91	34.09
15	13.69	300	66.39	33.61
16	12.54	310	67.13	32.87
17	12.52	320	67.77	32.23
18	14.48	330	68.23	31.77
19	14.38	340	68.47	31.53
20	16.37	350	70.34	29.66
21	12.98	432	81.13	18.87
22	13.90	1023	81.25	18.75
23	13.90	1100	81.60	18.40
24	13.84	1250	82.06	17.94
25	14.60	1300	82.54	17.46
26	14.60	1500	82.60	17.31
27	14.60	Melting point of platinum.	85.00	15.00

"Brands."

Red
Charcoal.

Black
Charcoal.

the oven, which is usually of the vertical type possessing a bottom outlet for the distillation products. The wood forming the lower layers of the charge is still giving off water when the

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upper zones are far beyond that stage and are already in a state of active carbonisation. It is only natural that this

THE CHEMICAL COMPOSITION OF CHARCOAL PRODUCED
AT VARIOUS TEMPERATURES (Violette).

No.	Temperature to which the wood was exposed. °C.	100 parts of the residues in the distillation vessels— “brands,” red charcoal, black charcoal—contained			
		Carbon. Parts.	Hydrogen. Parts.	Oxygen + Nitrogen, in- cluding loss. Parts.	Ash. Parts.
1	150	47.5105	6.1200	46.2900	0.0800
2	160	47.6055	6.0645	46.2710	0.0850
3	170	47.7750	6.1950	45.9535	0.0980
4	180	48.9360	5.8400	45.1230	0.1170
5	190	50.6145	5.1150	44.0625	0.2215
6	200	51.8170	3.9945	43.9760	0.2265
7	210	53.3735	4.9030	41.5380	0.2000
8	220	54.5700	4.1505	41.3936	0.2170
9	230	57.1465	5.5080	37.0470	0.3145
10	240	61.3070	5.5070	32.7055	0.5150
11	250	65.5875	3.8100	28.9670	0.6320
12	260	67.8905	5.0380	26.4935	0.5595
13	270	70.4535	4.6415	24.1920	0.8555
14	280	72.6395	4.7050	22.0975	0.5680
15	290	72.4940	4.9810	21.9290	0.6100
16	300	73.2360	4.2540	21.9620	0.5690
17	310	73.6330	3.8295	21.8125	0.7440
18	320	73.5735	4.8305	21.0860	0.5185
19	330	73.5515	4.6260	21.3330	0.4765
20	340	75.2020	4.4065	19.9620	0.4775
21	350	76.6440	4.1360	18.4415	0.6130
22	—	81.6435	1.9610	15.2455	1.1625
23	432	81.9745	2.2975	14.1485	1.5975
24	1020	83.2925	1.7020	13.7935	1.2245
25	1110	88.1385	1.4150	9.2595	1.1990
26	1350	90.8110	1.5835	6.4895	1.1515
27	1500	94.5660	0.7395	3.8406	0.6640
28	above 1500	96.5170	0.6215	0.9360	1.9455

large accumulation of strongly heated charcoal should have some effect on the adjacent portions of the charge, from which,

possibly, the water has only just been driven off. These portions of the charge, under the influence of the heat radiated from the charcoal and of that given up by the hot gases and vapours, pass rapidly into the distillation phase which then proceeds exothermically with violent evolution of gas.¹

A similar phenomenon also occurs in smaller carbonising apparatus as soon as the contents have reached a certain temperature—about 280° C. At this temperature, the wood is absolutely dry and conversion into charcoal sets in suddenly. The composition of the gas, which up to this point has consisted almost entirely of carbon dioxide and carbon monoxide, also changes owing to increased formation of hydrocarbons and hydrogen. The evolution of gas becomes extremely vigorous; the concentration of acetic acid in the distillate, which at first was low, rises suddenly to at least double its original value, and even if the furnace is drawn or the firing is reduced, the rate of flow of the distillate is very much greater than at any other stage of the process. This period, which originates without any doubt in an exothermic reaction, lasts, with small charges, from one to two hours, and with large charges, from four to six hours or even longer; it is then succeeded by a period of calmer distillation. The smaller the carbonising plant, the less marked is this phenomenon; the larger the plant, the more pronounced are the violent evolution of gas and the rapid flow of the distillate.

Hence, the distillation of wood in industrial-scale carbonising apparatus resolves itself into four different stages:—

1. Evaporation of the moisture present in the wood, as a result of the external application of heat. This process takes place at an average temperature of 170° C., and during this period scarcely any gas is formed.

2. Further heating of the wood to the temperature (270°–280° C.) necessary to initiate the exothermic reaction or period of “auto-carbonisation.” Gas consisting almost entirely of carbon monoxide and dioxide, is evolved and a certain amount of acetic acid is formed together with relatively small quantities of wood-naphtha and tar.

3. The exothermic period, which proceeds without any supply

¹ For detailed information on internal temperature relations for the various types of Swedish oven see “Om Kolning af Barrwed” by Hilding Bergström, (Stockholm, 1904.)

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of heat. During this period concentration of carbon in the charcoal takes place, and large quantities of hydrocarbons, acetic acid, wood-naphtha, and tar, are produced, while the temperature rises to 380°-400° C.

4. Cooling of the charcoal, possibly in an atmosphere of hydrocarbons in the carbonising apparatus itself. Under these conditions, hydrocarbons are adsorbed by the charcoal and condensed to more complex and less volatile compounds.

During the first and second periods, heat must be supplied from external sources; for the third period, however, little if any external heating is required, and conversely, this period furnishes the most valuable non-condensable and *combustible* gas. Obviously, this gas is produced at a stage when it is least useful for heating the particular apparatus from which it is derived, hence arrangements must be made to employ it for heating other carbonising apparatus which is at a different stage of the process. If the charge is only slowly heated at the beginning of the process and the first period is allowed to drag, the quantity of dry wood which accumulates in the plant is increased accordingly and as a result the action during the third period is more violent.

When the wood has reached a temperature of 270°-280° C. the period of active carbonisation sets in with extreme rapidity. For this reason it is essential that the method of firing should be such as to prevent the accumulation of large masses of dry wood. Precautions must therefore be taken to ensure that drying and carbonisation of the wood run side by side as far as possible. This actually takes place in all plant of relatively small diameter which is fitted with top vapour-outlets and heated externally. In the large American and Swedish plants, however, the conditions are different, for large masses of dry wood pass suddenly into the phase of "auto-carbonisation." In order to cope with the consequent rapid evolution of distillation products, a central condensing plant and a central gas-main must be provided, or, if each oven is fitted with its own condenser, the latter must be of sufficient size to deal with the disproportionately great output during this short period, and suitable arrangements must also be made for carrying off the non-condensable gas. After the violent period, distillation proceeds quietly again, and only gradual heating to 375°-400° C. is required to finish the

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process and to ensure a sufficiently high percentage of carbon in the charcoal.

The vigour of the reaction in a carbonising apparatus depends on the extent to which moisture is still present in the charge. The carbon-content of the charcoal is determined by the temperature at which the process is completed.

The reactions which take place during the carbonisation of resinous coniferous wood are described elsewhere. (See p. 70.)

CHAPTER IV

THE PRODUCTS OF DESTRUCTIVE DISTILLATION OF WOOD

Composition of Air-dry Wood.—Air-dry wood possesses the following approximate composition:—

	Per cent.
Carbon	40·0
Hydrogen	4·8
Oxygen	34·4
Ash	0·8
Water	20·0

Nature and Quantity of the Products.—Numerous data on the nature and quantity of the products obtainable from various species of wood may be found in the literature. These data are mostly based on experiments made in the laboratory, and the number of different results is just about as large as the number of experiments performed. This is readily explained by the fact that scarcely any other raw material in Nature is so unequal in character. Samples of wood taken at different levels from one and the same tree are never uniform. Still greater differences are shown by samples of wood of the same species and age taken from different localities; in fact, it is no exaggeration to state that even an individual piece of wood cannot be expected to exhibit the same properties throughout.

No other raw material is capable of exhibiting such wide variation in its chemical behaviour while remaining completely uniform in outward appearance and even in elementary composition.

The main factors governing the quantity of distillate obtainable from any particular kind of wood are: the species, the moisture-content, the relative proportions of cellulose and lignin—the latter alone producing methyl alcohol—the

ratio of actual wood-substance to air-pores (that is, the specific gravity of the wood), the soundness of the wood, the temperature of carbonisation, and finally the design or type of carbonising apparatus employed. It must not be forgotten that the efficiency of the stoker also plays an important part.

Taking into account all these continually changing factors the question arises as to how far it is possible to speak of a particular yield from a particular species of wood, or to guarantee that yield.

As a matter of fact it is impossible. All data regarding the yields obtainable from definite species of wood possess only local and relative significance. These figures are never absolute, and for this reason it is unsound to make use of them in predicting yields from the same species of wood, unless all the conditions under which the process of distillation is carried out are the same—a very unlikely circumstance.

Hence, it is always necessary to be cautious in using such data, especially in regard to *guaranteed yields* which no one can possibly give without having worked for years on one and the same wood, and even then only for the particular place at which those yields were obtained.

External Phenomena of Wood - Distillation.—We shall now consider, briefly, the external phenomena of the process of wood-distillation, employing for that purpose one of the simplest types of carbonising apparatus (Fig. 2).

This apparatus consists of a closed iron cylinder which lies in a furnace. The furnace gases circulate round the outside of the cylinder, which is connected by means of an outlet pipe with a condenser. It will be assumed that the hot charcoal from a preceding operation has just been withdrawn from the cylinder, and that the retort walls are at a dull red heat, only visible in the dark.

The retort is charged with split billets of hardwood, and the door is closed immediately. After five to ten minutes the retort neck becomes warm—a sign that the process of distillation has begun. Shortly afterwards the first portions of the distillate flow from the condenser and at the same time non-condensable gas is evolved, as yet only in small quantities and barely inflammable. This gas consists chiefly of air which has been driven out of the retort and of the wood itself by the action of heat. Practically from the outset the presence of acid may be detected in the liquid distillate, and after the air has been

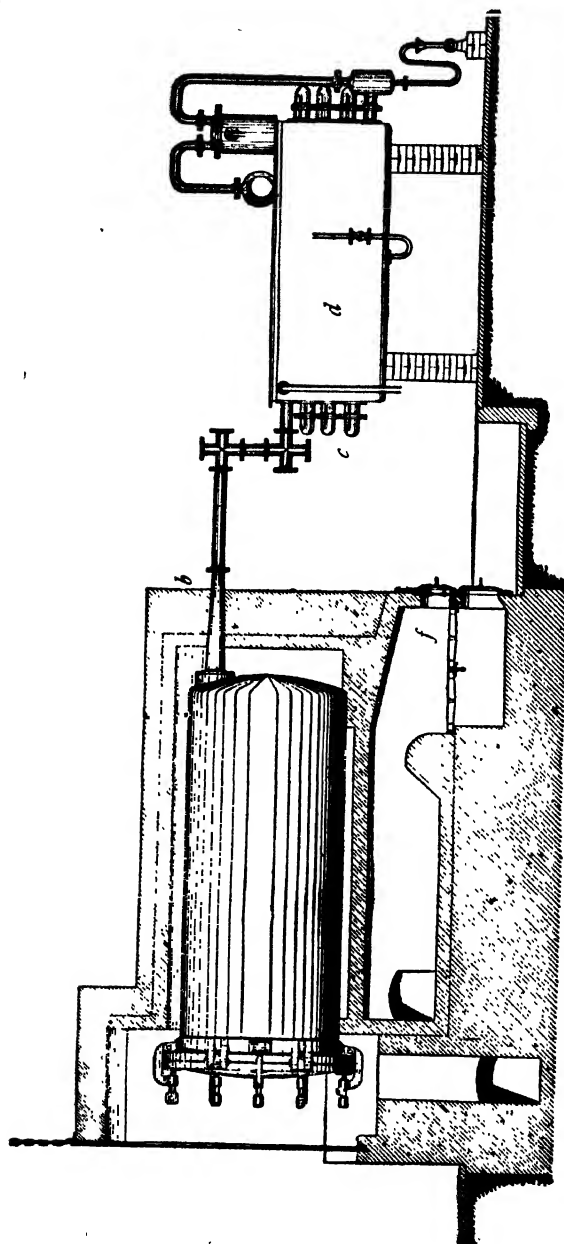


FIG. 2.—HORIZONTAL STEEL RETORT (CAPACITY, 1.5 STACKED CU. METRES ; OPERATING PERIOD, 12-16 HOURS.)
a, retort ; *b*, retort neck ; *c*, condenser tubes ; *d*, condenser tank ; *f* furnace.

expelled from the retort the non-condensable gas is found to consist of a mixture of carbon monoxide and dioxide. The simultaneous appearance of these products, so soon after the introduction of wood into the hot retort, demonstrates that the process of distilling wood under the above conditions does not consist in expulsion of the whole of the moisture in the first place, followed by carbonisation of the wood; on the contrary, energetic decomposition of those portions of the charge which are particularly exposed to the action of heat—namely, those pieces of wood which lie next to the hot retort-shell—begins immediately. At first, the distillate contains only very little acid and practically no tar. As the operation proceeds, larger quantities of non-condensable gas are produced; the acid-content of the brown aqueous distillate (pyroligneous acid) rises steadily; the colour of the distillate becomes darker; the amount of tar increases; and hydrocarbons and hydrogen take the place of carbon monoxide and dioxide in the gas. Finally, after about ten to twelve hours (with a charge of 2–4 cu. metres) the flow of distillate gradually comes to an end, the evolution of gas diminishes, and the retort neck becomes cold—an indication that the process is finished.

The fire is then drawn and the retort door is opened, with the result that the charcoal usually becomes ignited. The charcoal is discharged as rapidly as possible into iron boxes placed in front of the retort; the boxes are hermetically sealed, and the contents are allowed to cool. The retort is now ready for a fresh charge.

Products of Destructive Distillation.—The products of destructive distillation of hardwood are therefore:—

Wood-gas.

Pyroligneous Acid; a brown aqueous distillate.

Wood-tar; partly dissolved, partly suspended in the pyroligneous acid.

Charcoal.

These four products are also obtained when coniferous wood is carbonised, together with a *fifth* product which usually floats on the surface of the pyroligneous acid and is a mixture composed of *terpenes*, *products of the destructive distillation of rosin*, and *substances of a tarry nature*.

Quantities of Finished Products obtainable from Various Kinds of Raw Material.—Reference has already been made

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to the fact that wood is a raw material of widely varying constitution and properties. It is not surprising, therefore, to find that published yields of wood-distillation products differ very greatly, particularly when these yields are based on a bulk-measure (cord, stère, etc.) of which the weight is unknown, and when no information is given as to the moisture-content of the wood.

The author has in his possession very extensive information concerning yields given under practical conditions by various species of wood derived from many different countries.

Only a few isolated examples will be given here. These yields, which were obtained from retorts, refer to moisture-free wood and are expressed in percentages by weight.

Kind of wood, etc.	Charcoal.		Acetate of lime (80 %).		Crude naphtha. (100 %).		Tar.		Pine oil.	
	Observed		Observed		Observed		Observed		Observed	
	Max.	Min.	Max.	Min.	Max.	Min.	Max.	Min.	Max.	Min.
European beech . . .	33	28	10.5	8	2.5	1.7	6	5	—	—
American maple . . .	35	—	8	—	2	—	7	—	—	—
Pine, very rich in resin, from Georgia, U.S.A. .	33	28	2.5	2.3	0.42	0.28	20	—	8	—
European silver fir . .	36	33	3.6	3.0	0.8	0.6	12	6	5	0.4
Sawdust (softwood) . .	33	—	3	—	0.6	—	10	—	—	—
Olive stones from Spain .	35	—	4	—	1.2	—	4	—	—	—

Samples of wood from South America, Australia, and Africa gave yields which in some cases approached those from European softwood, and in others those from European beech ; in fact, the figures for certain African species exceeded the maximum figures for European beech.

CHAPTER V

THE NON-CONDENSABLE GAS: ITS COMPOSITION, PROPERTIES AND APPLICATION

Composition of Wood-Gas.—According to the investigations of F. Fischer,¹ the gaseous mixture, produced during the destructive distillation of wood in retorts under normal operating conditions, possesses the following composition. The figures represent the average of a large number of analyses and agree approximately with the author's own results :—

	Per cent by volume.
Carbon dioxide	59·0
Carbon monoxide	33·0
Methane	3·5
Hydrogen	3·0
Pyroligneous acid vapours, etc.	1·5

The rate of evolution of the various components is by no means uniform. At first, practically the only gaseous product is the air contained in the wood and in the retort. This is followed by gas consisting almost entirely of a mixture of carbon monoxide and dioxide, and barely inflammable. Only after the wood has completely given up its moisture does the flow of gas become very vigorous—usually quite suddenly: at the same time the acetic acid content of the pyroligneous acid rises, likewise rather abruptly, and the gas burns readily owing to its richness in hydrocarbons. At a later stage of the process, the rate of flow decreases, but the combustibility of the gas does not diminish.

At the beginning of the distillation, a limited amount of air may be regarded as a normal component of the wood-gas, but the proportion of air may easily become excessive if suction fans are used to withdraw the gas, and the carbonising

¹ Dingl. polyt. Journ., 1880, **238**, 55.

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apparatus, delivery pipes, etc., are not absolutely gas-tight. The author, on one occasion, analysed wood-gas which had been produced under these unfavourable conditions and found that it possessed the following average composition :—

	Per cent. by volume
Carbon dioxide	36
Carbon monoxide	20
Oxygen	6
Nitrogen, etc.	38

On the other hand, the wood-gas produced on carbonising green oak in the large Meyer retorts (capacity, 25 cubic metres; operating period about 20 hours), and withdrawn by suction, showed, during the period of most vigorous evolution, the following composition :—

	Per cent by volume.
Carbon dioxide	35·5
Oxygen	0·5
Carbon monoxide	47·5
Hydrocarbons, hydrogen	16·5

Saturation of Wood-Gas with Distillation Products.—

The gas issuing from the separator attached to the condenser contains other abnormal constituents apart from air—namely, components of pyroligneous acid and tar—with which it is more or less saturated according to the temperature of the cooling water and the pressure prevailing in the condenser tubes.

Exact data in respect of the saturation of wood-gas with components of pyroligneous acid, etc., are not available, but for the present purpose we may assume that the relations are similar to those existing between air and water vapour. Assuming that the air becomes completely saturated, the following volumes are required for the absorption of 1 kilo of water vapour :—

	57·0 cubic metres of dry air at 20°C.
1	43·5 " " " 25°C.
	32·5 " " " 30°C.

Hence, the greater the quantity of gas formed during the carbonisation process and the higher the temperature at which it leaves the retort condensers, the greater is the loss of acetic acid and more especially of wood-naptha.

It follows, therefore, that :—

1. The quantity of gas which results from the carbonisation of wood should be kept down to a minimum by operating the process at the lowest possible temperature.

2. The condensers must be capable of cooling the gas, before its exit, to the temperature of the cooling water, which should not exceed 20° C.

3. Influx of air into the carbonising apparatus, etc., should be prevented, otherwise the volume of gas is considerably increased and losses due to oxidation—especially of methyl alcohol—also result.

Calorific Value of Wood-gas.—We have now to ascertain the manner in which the non-condensable gas, which represents 15–20 per cent of the original weight of wood, may be utilised to the best advantage. In order to settle this question it is necessary to determine the calorific value of the gas on the basis of its composition. Accepting Fischer's figures for the average composition of normal wood-gas obtained from retorts, namely :—

		Per cent by volume.
Carbon dioxide	59.0
Carbon monoxide	33.0
Methane	3.5
Hydrogen	3.0
Pyroligneous acid (reckoned as water vapour)		1.5

we obtain the following data :—

Com- ponents.	Mols. in 1 mol. of wood- gas. <i>m</i>	Molecu- lar weight. <i>u</i>	Grams in 1 molal volume of wood- gas. <i>m</i> × <i>u</i>	Calorific value <i>H</i> for 1 cu. metre at 15°C and 1 atm. at constant pressure. Kilo-calories.	Calorific value per volume <i>m</i> <i>m</i> × <i>H</i>	Parts by volume of oxygen necessary for combustion.	
						Per 1 part by volume.	Per volume. <i>m</i>
CO ₂	0.590	44	25.96
CO	0.330	28	9.24	2800	924.0	0.5	0.5 × 0.33 = 0.165
CH ₄	0.035	16	0.56	8700	304.5	2.0	2.0 × 0.035 = 0.070
H ₂	0.030	2	0.06	2810	84.3	0.5	0.5 × 0.03 = 0.015
H ₂ O	0.015	18	0.27
	1.000		36.09		1312.8		0.250

Hence the calorific value of wood-gas of the above composition, per 1 cu. metre at 15° C. and 1 atm. pressure = 1312.8 kilo-calories.

Since 1 gram mol of every gas at 15° C. and 1 atm. occu-

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pies 23.6 litres, it follows that the weight of 1 cu. metre of wood-gas under the same conditions = $\frac{36.09}{23.6} = 1.530$ kilos, and

that the density compared with air = $\frac{36.09}{29} = 1.244$.

In order to calculate the *practical* calorific value of the gas it is necessary, in the first place, to ascertain the quantities of the products resulting on combustion. According to the above table 1 cu. metre of the gas requires, theoretically, 0.250 cu. metre of oxygen. In practice, however, this amount of oxygen is insufficient; actually, about 170 per cent of this figure, viz. 0.425 cu. metre, is necessary, corresponding to $\frac{0.425}{0.210} = 2.023$ cu. metres of air.

On combustion :—

1 vol. CO produces 1 vol. CO₂.

1 vol. CH₄ produces 1 vol. CO₂ and 2 vols. water vapour.

1 vol. H produces 1 vol. water vapour.

Hence, as a result of the combustion of 1 cu. metre of wood-gas of the above composition we obtain :—

	Cubic metres.
CO ₂ = 0.59 + 0.33 + 0.035	= 0.950
H ₂ O = 0.015 + 0.03 + 2(0.035)	= 0.115
O = (0.21 × 2.023) - 0.250	= 0.175
N = 0.79 × 2.023	= 1.598

at 15° and 1 atm.

2.838

The amount of water produced by the combustion of 1 cu. metre of wood-gas = 0.03 + 2(0.035) = 0.1 cu. metre. Since this amount of water must be vaporised, the number of kilocalories necessary for the purpose must be deducted from the above *higher* calorific value. The *lower* calorific value, therefore, amounts to :—

$1312.8 - 0.1 \times \frac{18}{23.6} \times 600 = 1267.0$ kilo-calories per 1 cu. metre of wood-gas at 15° C. and 1 atm.

The practical calorific value of the gas is still further reduced however owing to the relatively high content of carbon dioxide which causes a correspondingly great loss of heat in the flue gases. Assuming that the temperature of the flue

gases leaving the furnace is only 320°C. , and that the *mean* specific heat (at constant pressure) of 1 cu. metre of both nitrogen and oxygen measured at 15° and 1 atm. = 0.29, and of both water vapour and carbon dioxide = 0.37, then the loss of heat on burning 1 cu. metre of wood-gas is made up as follows :—

	Kilo-calories.
$\text{CO}_2 = 0.950 \times 0.37 \times (320 - 20) =$	105.45
$\text{H}_2\text{O} = 0.115 \times 0.37 \times (320 - 20) =$	12.76
$\text{O} = 0.175 \times 0.29 \times (320 - 20) =$	15.22
$\text{N} = 1.598 \times 0.29 \times (320 - 20) =$	139.02

Total = 272.45

Deducting this value from the *lower* calorific value of the wood-gas :—

$$1267.0 - 272.45 = 994.55 \text{ kilo-calories,}$$

the difference gives us the actual calorific value of 1 cu. metre of the gas exclusive of radiation losses ; assuming that the latter amount to 6 per cent, the final value is 935 kilo-calories per 1 cu. metre of wood-gas at 15°C. and 1 atm.

The maximum yield of wood-gas from 100 kilos. of wood is 20–25 kilos., equivalent to about 15 cu. metres ; and the actual calorific value of 15 cu. metres = $935 \times 15 = 14,025$ kilo-calories.

Reckoning the amount of heat actually utilised in practice per 1 kilo. of good quality coal at 5000 kilo-calories, it follows that the wood-gas derived from 100 kilos. of air-dry wood possesses the same fuel value as $\frac{14,025}{5000} = 2.8$ kilos. of coal (cal. val. = 7000 kilo-calories).

It has been shown above that the heat lost in the flue gases amounts to about 21 per cent of the available heat in the gas.

If the wood-gas before combustion were preheated to the exit-temperature on the regenerative principle, its actual calorific value would be increased correspondingly ; thus the fuel value of the wood-gas from 100 kilos. of wood would be equal to that of 3.6 kilos. of coal, instead of 2.8 kilos. Since about 7.5 kilos. of coal are consumed in carbonising 100 kilos. of wood, it follows that by preheating the wood-gas to about 300° before combustion, the consumption would be reduced by approximately 10 per cent. Assuming that the gas can be preheated to a sufficiently high temperature practically without cost, the advantage is obvious.

The above figures show that the wood-gas possesses considerable value as a fuel. Judging from its composition the gas would also appear to be suitable for power purposes, especially in view of the successful results obtained with blast furnace gas.

We have seen that the lower calorific value of 1 cu. metre of wood-gas = 1267.0 kilo-calories and that, *theoretically*, 0.250 cu. metres of oxygen = $\frac{0.250}{0.21} = 1.19$ cu. metres of air are required for its combustion.

The lower calorific value of 1 cu. metre of the *combustible mixture* (1 + 1.19 cu. metres) = $\frac{1267.0}{2.19} = 578$ kilo-calories. The calorific value of blast furnace gas under the same conditions = 560 kilo-calories.

If these mixtures are introduced into gas engines of the same size, the power output will be proportional to the calorific value of the gaseous mixture, assuming that the degree of combustion is the same. Hence the power value of the wood-gas compared with that of the blast furnace gas is as 578 : 560, or $\frac{578 \times 100}{560} = 103$ per cent of that of the blast furnace gas.

Modern gas engines consume from 2.8 to 3.7 cu. metres of blast furnace gas per 1 H.P. hour, according to the size of the engine. The mean amount, namely, 3.25 cu. metres, is equivalent therefore to $\frac{3.25 \times 100}{103} = 3.15$ cu. metres of wood-gas.

One hundred kilos. of wood produce about 15 cu. metres of wood-gas, which are equivalent to $\frac{15 \times 1}{3.15} = 4.76$ H.P. hour.

If steam is used instead of gas, and we assume that only 15 kilos. of steam = $\frac{15}{7} = 2.14$ kilos. of good quality coal are required per 1 H.P. hour, then the cost of generating 4.76 H.P. hour, reckoning the price of coal at 15s. per metric ton = $\frac{4.76 \times 2.14 \times 15}{1000} = 0.15s.$

The fuel value of the wood-gas per 100 kilos. of wood is equal to only 2.8—3.6 kilos. of coal at 0.015s. per kilo. = 0.048s.

From this comparison it follows that the wood-gas can be

utilised more advantageously for power purposes than for heating purposes, assuming that there is no application for the exhaust steam from steam engines.

Whatever the purpose to which the gas is applied, it cannot be used directly in the condition in which it leaves the retort condensers. As mentioned above, the gas is more or less saturated with the components of pyroligneous acid, especially wood-naphtha, according to the exit-temperature and the pressure prevailing in the condenser tubes.

Fifteen cu. metres of the gas at 20° C. will contain, when fully saturated, about 260 grams of these components, assuming that the latter behave like water and the gas like air. In actual fact the degree of saturation is higher owing to the highly volatile nature of certain of the components of pyroligneous acid; consequently the gas may give rise to considerable loss of valuable products, and if used directly in a gas engine it will cause corrosion since it contains free acetic acid.

In order to avoid these difficulties, the wood-gas, as it leaves the retort condensers, is passed by means of a fan through scrubbers of suitable dimensions; in these the components of pyroligneous acid are removed by washing with water, their place being taken by water vapour.

The scrubbed gases are then either preheated and used as fuel in the retort furnaces, boiler furnaces, etc., or else employed in a gas engine for generating power; or they may be used for both purposes.

One hundred kilos of wood will produce wood-gas equal in fuel value to about 3 kilos. of coal and possessing a power value of 4.76 H.P. per hour (approximately 10 kilos. of coal). If used entirely for generating power, a saving of about 7 kilos. of coal per 100 kilos. of wood is effected.

CHAPTER VI

PYROLIGNEOUS ACID AND ITS COMPOSITION

PYROLIGNEOUS acid is obtained, during the destructive distillation of wood, as a brown liquid possessing a characteristic odour. This product, mixed with the tar, flows from the condenser connected with the carbonising apparatus, and is separated from the main bulk of the tar, which is mostly of higher specific gravity, simply by settling. It should be noted that the tar derived from coniferous wood, and from certain other species of wood which produce comparatively large quantities of light oils, is of lower specific gravity than the acid.

The chief component of pyroligneous acid is water, which is derived partly from the moisture originally present in the wood, but mainly from the decomposition of the wood-substance during destructive distillation.

The amount of water present in pyroligneous acid (see table, p. 63) varies between 80 and 90 per cent according to the moisture-content and nature of the wood from which the acid has been derived.

The remaining components—amounting to 10–20 per cent—consist of organic compounds belonging chiefly to the aliphatic series. The following substances have been identified in the pyroligneous acid and tar by the under-mentioned authors :—¹

Anderson, Chem. News, 1866, **14**, 257; Polyt. Journ., 1867, **183**, 242.

Barré, Compt. rend., 1869, **68**, 1222; Jahresber., 1869, **22**, 515.

Krämer and Grodsky, Ber., 1878, **11**, 1356; 1876, **9**, 1920.

Heill, Ber., 1877, **10**, 936.

Boyle, Kopp, "Geschichte der Chemie," Vol. IV, p. 329.

Taylor, Phil. Mag., 1822, **60**, 315.

Dumas and Peligot, Ann. Chim. Phys., 1835 [2], **58**, 5; 1836, **61**, 193. Ann. Chem., 1835, **15**, 1.

Aronheim, Ber., 1874, **7**, 1381, 1618.

¹ See "Muspratt's Chemie," Vol. II, p. 1870 (1889).

- Krämer and Grodsky*, Ber., 1874, **7**, 1492.
Völckel, Ann. Chem., 1853, **86**, 71.
V. Meyer, Ber., 1878, **11**, 1870.
Hill, Chem. Zentr., 1889, **1**, 508.
Dancer, Ann. Chem., 1864, **132**, 240.
Grodsky, Ber., 1884, **17**, 1369.
Buchner, Ann. Chem. 1855, **96**, 186.
Scanlan, Journ. prakt. Chem., 1836 [1], **7**, 94.
Apjohn and Gregory, Journ. prakt. Chem., 1838 [1], **13**, 70.
Schweizer, Journ. prakt. Chem., 1848 [1], **44**, 129.
Camille, Lorrin, Jahresber., 1873, **28**, 686.
Vincent, Chem. Zentr., 1873 (Ser. 3), **4**, 259, 725.
Cahours, Ann. Chem., 1850, **76**, 286.
Knauss, Fehling, Ann. Chem., 1858, **106**, 388.
Fritzsche, Ann. Chem., 1859, **109**, 250.
Bamberger and Hooker, Ann. Chem., 1885, **229**, 102.
Eckstrand, Ann. Chem., 1877, **185**, 75.
Berthelot, Jahresber., 1867, **20**, 599.
Reichenbach, Schweigger-Seidel's Journ. Chem. Phys., **59**, 436; **61**, 175, 273; **62**, 129; **65**, 461; **66**, 301, 318, 345; **67**, 1, 57, 274; **68**, 1, 57, 295, 351, 399; **69**, 175, 241.
Reichenbach, Journ. prakt. Chem., 1831 [1], **1**, 1.
Reichenbach, Berzelius' Jahresber., 1836, **15**, 408.
Runge, Ann. Phys., 1834, **31**, 69.
Laurent, Ann. Chim. Phys., 1841 [3], **3**, 195.
v. Gorup-Besanez, Ann. Chem., 1853, **86**, 223; 1867, **143**, 129.
Hlasiwetz, Ann. Chem., 1858, **106**, 339.
H. Müller, Zeit. Chem. Pharm., 1864, 703.
Tiemann and Mendelsohn, Ber., 1875, **8**, 1136; 1877, **10**, 58.
Marasse, Ann. Chem., 1869, **152**, 59.
Tiemann and Koppe, Ber., 1881, **14**, 2005.
A. W. Hofmann, Ber., 1878, **11**, 329, 1455; 1879, **12**, 1371, 2216.
Liebermann, Ber., 1876, **9**, 334.

(a) Present chiefly in the pyroligneous acid :—

Formic acid.	Furfural.
Acetic acid.	Methyl furfural.
Propionic acid.	Acetone.
Butyric acid.	Methyl ethyl ketone.
Valeric acid.	Ethyl propyl ketone.
Caproic acid	Dimethyl acetal.
Crotonic acid.	•Methylal.
Angelic acid.	• Valerolactone.
Pyromucic acid.	• Methyl acetate.
Methyl alcohol.	Pyrocatechol.
Allyl alcohol.	Ammonia.
Acetaldehyde.	Methylamine.

(b) Present chiefly in the tar :—

Benzene.	Chrysene.
Xylene.	Paraffin.
Cumene.	<i>Terpenes</i> (coniferous wood).
Cymene.	<i>Creosote</i> .
Retene.	

In addition, the following products were isolated by Reichenbach :—

Eupion.	Picamar.
Mesit.	Pittakall.
Kapnomor.	Cedriret.

The constitution of certain of these products has since been established ; the chemical individuality of others is doubtful.

As far as the actual process is concerned, only those products, which are indicated by italics in the above lists claim attention, since they represent either final objects of manufacture or substances which must receive special consideration in the course of the process.

The remaining products possess only scientific interest.

The essential components of crude pyroligneous acid are therefore *water, dissolved tar, acetic acid and its homologues and wood-naphtha*, the last consisting of a mixture of methyl alcohol, allyl alcohol, acetone, aldehydes, methyl acetate, ammonia, amines and higher ketones.

The components of pyroligneous acid may be separated into two groups according to their volatility :—

(a) *Non-volatile at the boiling-point of pyroligneous acid :*

Tarry products,

(b) *Volatile at the boiling-point of pyroligneous acid :—*

Neutral : Water.

Acid : Acetic acid and its homologues.

Basic : Ammonia and amines.

Alcohols, aldehydes, esters and ketones : Methyl alcohol, allyl alcohol, acetaldehyde, furfural, methyl acetate, acetone and higher ketones.

The proportions in which these different sets of components are present vary considerably according to the species of wood, the moisture-content of the wood, the rate and temperature of distillation, etc.

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This may be illustrated by comparing the average composition of 100 kilos. of pyroligneous acid from two different sources :-

	Pyroligneous acid from air-dry beechwood.	Pyroligneous acid from air-dry coniferous wood.
1. Water . . .	81 kilos.	91 kilos.
2. Components of wood-naphtha	3 kilos. (including 0.56 kilo. of acetone)	1.5 kilos. (including 0.28 kilo. of acetone)
3. Acetic acid and homologues, determined in <i>distilled</i> pyroligneous acid and calculated as acetic acid . . .	7-9 kilos.	3.5 kilos.
4. Ammonia and its derivatives . . .	Traces	Traces
5. Dissolved tarry matter	kilos. & upwards	4 kilos.

Owing to the large amount of water present in crude pyroligneous acid it is impracticable to transport the product over any great distance. Moreover, there is no application for any considerable quantity of the crude acid, or even for the distilled, tar-free acid.¹ In consequence, wood-distillers have always been compelled to isolate the more valuable components—acetic acid and wood-naphtha—in concentrated form, in order to facilitate the subsequent conversion of these products into pure acetic acid, acetone, methyl alcohol, formaldehyde, etc. This concentration process is all the more necessary in view of the fact that subsequent treatment of the products is not always undertaken by the factory at which they originate.

On considering the boiling-points of acetone (56° C.), methyl alcohol (66° C.), water (100° C.), acetic acid (118° C.) and tar (above 200° C.), it would appear possible to resolve pyroligneous acid into its components by fractional distillation. This proves correct as regards the separation of *wood-naphtha* from water, acetic acid and tar, and also the separation of the *mixture* of wood-naphtha, water and acetic acid

¹ *Acetum pyrolignosum rectificatum*, German Pharmacopœia (D.A.B. V).

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from the tar. Separation of wood-naphtha and elimination of tar from crude pyroligneous acid can be readily effected by either simple or fractional distillation, and this method is actually employed in practice.

Unfortunately, however, no suitable process of fractional distillation—either with or without addition of salt and at a reasonable cost—has yet been introduced for converting an aqueous solution of acetic acid containing less than 10–12 per cent into concentrated acetic acid (e.g. 50 per cent) and water. All attempts in this direction, even the most recent, have been unsuccessful, for not only is the cost of the process out of all proportion to the concentration attainable, but the quality of the concentrated product is by no means satisfactory. Hence, it is the custom in wood-distillation factories to isolate acetic acid, not in the form of concentrated *crude acid*, but as a *solid acetate* containing the greatest possible quantity of the pure salt. In this connection only two products come into consideration, namely, *calcium acetate*¹ and *sodium acetate*.

If crude pyroligneous acid consisted only of acetic acid, wood-naphtha and water, its subsequent treatment would be very simple. Unfortunately, however, dissolved tar is always present in the pyroligneous acid and remains in the solid acetate unless it is removed before the acid is neutralised.

One hundred kilos. of beechwood pyroligneous acid contain 9 kilos. of acetic acid, which, on neutralisation with milk of lime, should produce

$$60 : 79 :: 9 : x = 11.85 \text{ kilos.}$$

of calcium acetate (100 per cent). But 100 kilos. of the pyroligneous acid contain 7 kilos. of dissolved tar, most of which remains mixed with the solid acetate obtained after the neutralised solution has been evaporated to dryness. The total weight of the product is therefore $11.85 + 7 = 18.85$ kilos., and since only 11.85 kilos. of pure calcium acetate are present, the product contains only 63 per cent. In practice it is certainly possible, after partial separation of the tar by mechanical means, to manufacture acetate of lime ("brown acetate") containing 67 per cent of calcium acetate by direct neutralisation of crude pyroligneous acid. But even in this case the very

¹ Certain factories in England and Scotland convert their crude pyroligneous acid into acetate of iron ("iron liquor"). Details of this process will be found in Chap. XV, p. 288.

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important influence of the tarry products dissolved in crude pyroligneous acid on the purity of the solid acetate is still evident.

For this reason one of the most important operations in any wood-distillation factory is to remove the dissolved tar from the pyroligneous acid by some practicable method, so as to render possible the production of acetate of lime free from tarry matter and containing at least 80 per cent of pure calcium acetate.

CHAPTER VII

WOOD-TAR AND ITS COMPONENTS

THE designation "Tar," which is applied to one of the liquid products of wood-distillation, is difficult to define; but it is understood to refer to a group of chemical products which possess many similarities both in external appearance and in chemical composition.

Wood-tar, unlike coal-tar and lignite-tar, contains only small quantities of ammonia derivatives, naphthalene and paraffin; the place of ammonia derivatives is taken by acids of the formic acid series, aliphatic alcohols, aldehydes and ketones.

It may be assumed that the tar travels from the carbonising apparatus to the condenser in the form of vapour or mist carried along by the current of hot non-condensable gas. Simultaneous condensation of tar and pyroligneous acid takes place in the tubes of the condenser, and both products, during the process of condensation and while flowing through the comparatively long tubes, have ample time and opportunity for mutual interchange of certain of their components.

The tar possesses a definite solvent power and consequently takes up a considerable quantity of acetic acid and its homologues; conversely, pyroligneous acid, in virtue of its content of acetic acid and wood-naphtha, extracts certain substances from the tar.

As a result of this interchange, the crude pyroligneous acid, on issuing from the condensers, contains tar *in solution* as well as in suspension. The higher the content of acetic acid and wood-naphtha in the pyroligneous acid, the greater is the amount of tar present in solution.

Tar derived from hardwood is for the most part heavier than pyroligneous acid. Consequently, when the mixture is allowed to stand, the tar settles below the acid as a brownish

black, more or less viscous liquid. Tar derived from resinous softwood is lighter than pyroligneous acid, and separates mostly above the acid owing to the presence of terpenes often in considerable quantities.

The tar obtained by allowing crude pyroligneous acid to settle is known as *settled tar*; it constitutes one of the varieties of tar produced by wood-distillation factories.

Pyroligneous acid, after being settled, is free from suspended tar, but still contains tarry matter in solution. On distilling the settled acid a residue remains in the still and constitutes another variety of tar, known as *residual* or *dissolved tar*.

Hardwood-tar—whether “settled” or “residual”—is always looked upon as a somewhat undesirable by-product. On the other hand, the tar obtained by distilling coniferous wood, especially highly resinous root-stumps or trunkwood, from which the sapwood has been removed, is often the main product of manufacture. An example of this class of raw material is the rootwood from the richly resinous long-leaf pine (*Pinus palustris*), a conifer which flourishes to a wide extent in Georgia, Virginia, Alabama, etc., U.S.A., and serves for the production of oil of turpentine. In some countries, for example Russia, Finland and Sweden, coniferous wood is distilled in a more or less primitive manner, solely for the purpose of producing tar.

Hardwood-tar varies in colour from brownish black to black, but softwood-tar of good quality, when spread out in thin layers, exhibits a golden-yellow colour, sometimes with an orange shade. The lighter the colour of softwood-tar when spread out on wood, the less it darkens on drying, and the more resinous and sticky its nature, the more highly is it valued.

Hardwood-tar seldom costs more than 2s. 6d. to 3s. per 100 kilos., and is difficult to sell. Good softwood-tar, which is used as ship's paint, for tarring ship's cables, ropes, etc., can readily be sold for 10s. to 15s., or even more, per 100 kilos.

Russia, Finland, Sweden, Silesia and West Prussia are the chief purveyors of softwood-tar, which is usually produced in some type of kiln or even in simple charcoal pits. It comes on the market, especially from Sweden, in a special form of barrel.

Hardwood-tar might be described as “greasy,” and softwood-tar as “sticky.”

Settled Hardwood-Tar.—The chief components of hard-wood-tar have already been tabulated on page 62. It is unnecessary to enter into particulars of all the components, since most of these are of scientific rather than of practical importance.

As far as the author is aware, no ultimate analyses of hard- or softwood-tar have yet been carried out, or, at least, no results have been published. In any case, such analyses would scarcely have much value, owing to the widely varying composition of the tar.

The components of hardwood-tar which possess most importance from the practical point of view are :—

Acetic acid and its homologues	
Methyl alcohol	
Methyl acetate	Components of wood-naphtha,
Acetone	

since these products must always be extracted from the tar on account of their value. Next in importance are the *heavy oils*, which are obtained on distilling wood-tar by direct fire. These oils contain the main bulk of the creosote together with other phenols. The remaining components of the tar—paraffin, hydrocarbons and pitch—are of very little interest to the wood-distiller at the present day; these products are now furnished exclusively by coal-tar and lignite-tar distillers, at prices which render competition on the part of the wood-tar distiller impossible.

Settled tar from beechwood possesses the following approximate composition :—

	Per cent.
Acetic acid.	2·00
Wood-naphtha	0·65
Water	17·75
Light oils (sp. gr. 0·97)	5·00
Heavy oils („ 1·043)	10·00
Wood-pitch	62·00
Gas, etc.	2·40
Specific Gravity = 1·08 at 15° C.	

In practically all cases, subsequent treatment of the tar is confined to the recovery of acetic acid and wood-naphtha; the residue, which still contains small quantities of water-soluble components and light oils together with the whole of

the heavy oils and pitch, is then put on the market as *dry tar* (*boiled tar*), or is used as fuel.

Only very rarely is the tar distilled down to pitch for the purpose of recovering the heavy oils; these are then sent to special factories to be worked up into pure creosote.

Dissolved or Residual Tar.—In outward appearance dissolved tar scarcely differs from settled tar, but its composition is entirely different. There is no essential difference however between the dissolved tar derived from hardwood and that from softwood.

Dissolved tar is always left as a residue in the still after the distillation of crude pyroligneous acid. As previously mentioned, the tar must be eliminated from the acid, if acetate of lime containing 80 per cent of calcium acetate is an object of manufacture.

Dissolved tar is probably formed (see page 199) from volatile components of pyroligneous acid such as aldehydes and phenols, as a result of secondary reactions—polymerisation, condensation, etc. In view of its general behaviour it must be regarded as a product of the nature of aldehyde-resin rather than as tar in the strict sense. This view is supported by its solubility in water and its general behaviour on distillation.

Although towards the end of the distillation of pyroligneous acid with high-pressure steam, dissolved tar is exposed to a temperature of about 150° C., it still retains a considerable quantity of acetic acid, as shown by the following figures which were obtained for a well-finished sample:

100 kilos. on distillation by direct fire gave:—

40 kilos. of aqueous distillate containing 20·4 per cent of acetic acid.

60 kilos. of brittle hard pitch of rusty appearance.

Hence, the tar contained:—

	Per cent.
Acetic acid.	8·16
Water	31·84
Brittle hard pitch	60·00

On comparing these results with the figures for settled tar from beechwood, the most striking features are the complete absence of light and heavy oils, and the high content of acetic acid and water.

As already mentioned, this variety of tar is moderately soluble in water, and for that reason alone it cannot be put to the same uses as settled tar, which may be used for water-proofing purposes; moreover, the high acetic acid content prohibits its use as a paint.

In some cases dissolved tar is burnt directly, or is mixed in certain proportions with settled tar. Usually, however, the product is distilled, either by direct fire or by injecting live steam and heating at the same time with indirect steam in order to recover acetic acid.

Tar Obtained by the Meyer Tar Separator.—The composition of the tar which is extracted from the volatile distillation products by means of the author's patent tar separator,¹ prior to the condensation of pyroligenous acid, lies between that of settled tar and that of dissolved tar. A sample on analysis gave :—

	Per cent.
Acetic acid	5
Water	16
Heavy oils	24
Medium pitch	55

Softwood-Tar.—The tar obtained by the destructive distillation of softwood in retorts is naturally very different from hardwood-tar. The latter is formed by the destructive distillation of cellulose and lignin. Softwood-tar is also formed by the destructive distillation of cellulose and lignin, but in softwood these substances are permeated by "turpentine," a mixture of oil of turpentine and rosin (colophony).

In distilling softwood it is necessary to distinguish between *three* successive, though to some extent overlapping, processes :—

1. Volatilisation of the oil of turpentine, present originally in the wood, by the steam generated from the moisture in the wood.
2. Destructive distillation of cellulose and lignin, whereby acetic acid, wood-naphtha, tar and charcoal are formed.
3. Destructive distillation of the rosin present in the wood, resulting in the formation of rosin-spirit and rosin-oils, which become mixed with the products of the first and second processes.

¹ German patent 189,303.

When vertical retorts with the vapour outlets at the bottom are employed, as is practically always the case for softwood, and when the wood undergoing carbonisation is highly resinous, a *fourth* process may occur, namely, that the rosin is melted directly out of the wood and mixes with the distillates.

When large quantities of softwood are carbonised in one operation and the turpentine-content of the wood is not too low, it is possible to obtain oil of turpentine as a separate product, or at the most only slightly contaminated with tar.

In opposite conditions the period during which oil of turpentine is vaporised coincides more or less with the period during which rosin is decomposed. In consequence, the products of rosin-distillation (rosin-spirit or pinoline, rosin-oils) become mixed with the oil of turpentine and the ordinary components of tar. The mixture leaves the condenser as "tar," and if the content of terpenes and rosin-oils is small, the product differs very little from hardwood-tar.

The extent to which terpenes, pinoline and rosin-oils are present in softwood-tar is indicated by the specific gravity of the product.

Softwood-tar which separates beneath pyroligneous acid contains little *pine-oil* (a mixture of oil of turpentine and light rosin-oils) and subsequent treatment for the recovery of that product is seldom profitable.

Distillation of softwood-tar down to pitch is no longer carried out, since the tar itself finds a ready market and is highly valued as a paint on account of the presence of rosin-distillation products and possibly undecomposed rosin which has been melted out of the wood.

Formerly, softwood-tar was distilled for the purpose of manufacturing brewers' pitch and cobblers' wax. Nowadays, these products are obtained more cheaply and of better quality from colophony, and the use of wood-tar as raw material has long been abandoned.

As a rule, treatment of softwood-tar for the removal of water, or rather of acid, is not undertaken unless it is also desired to regulate the viscosity of the tar by distilling off the *pine-oil*, or to recover the *pine-oil* from the tar.

The following data on the composition of softwood-tar were obtained by the author during the destructive distillation of Swedish spruce (sawmill waste) of low resin-content in

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vertical retorts of 30 cu. metres capacity, with the vapour outlet at the bottom :—

Time of taking sample.	Specific gravity at 15 °C.	Aqueous distillate. Per cent.	Light oils (oil of turpentine, phenols, hydrocarbons). Per cent.	Heavy oils (specific gravity above 1.000). Per cent.	Soft pitch (including loss). Per cent.
At the beginning of the distillation .	0.9245	below 1	64	7	23
In the middle of the distillation .	1.0340	9	28.6	20	42.4
At the end of the distillation .	1.0940	17	4.33	21	57.67

An essentially different composition was exhibited by tarry distillates from *Pinus palustris* ("light wood") obtained by the author in a factory in Georgia, U.S.A. These distillates were collected in three fractions, according to their specific gravity : the first up to 0.950 at the beginning of the distillation ; the second from 0.950 to 0.975, in the middle ; and the third from 0.975 upwards at the end.

1 $\frac{1}{16}$ cord (=4.0 cu. metres) of this wood weighed 1800 kilos. and gave :—

Weight of fraction. Kilos.	Specific gravity at 15 °C.	Aqueous distillate (pyroligneous acid). Per cent.	Terpenes, hydrocarbons, phenols. Per cent.	Softwood-tar, free from water and acid. Per cent.
<i>Fraction 1</i> : 173 kilos.=9.6 per cent of the original weight of wood . . .	Up to 0.950	11	70	19
<i>Fraction 2</i> : 54 kilos.=3 per cent of the original weight of wood . . .	0.950–0.975	16	45	39
<i>Fraction 3</i> : 400 kilos.=22 per cent of the original weight of wood . . .	above 0.975	14	10	76

CHAPTER VIII

CHARCOAL AND ITS COMPOSITION

CHARCOAL always forms the residue from the destructive distillation of wood in closed vessels, and is often the most important product of manufacture.

To carbonise wood without recovering the by-products is a perfectly reasonable proposition ; but it is very rarely sound to carbonise wood and at the same time to recover the by-products, if the value of the charcoal, whether intended for general purposes or simply as a fuel, does not at least cover the cost of the wood carbonised.

In very richly wooded countries which possess no industries, it may happen that there is no application for charcoal except as fuel ; in that case its value must cover the purchase-price of the wood required for its production.

As a general rule, however, this position does not arise ; on the contrary, charcoal still forms an important product of every wood-distillation factory, in spite of the enormous increase in the value of the by-products.

Formerly, charcoal was produced almost entirely in "meilers," and was used on a very large scale in the manufacture of iron. In many countries, especially Germany, coke has almost completely displaced charcoal in the iron industry, but in certain parts of the United States, in the Urals, in Hungary, Sweden and Bosnia, considerable quantities of charcoal are still used in that industry.

Sweden particularly consumes vast amounts, of which more than 90 per cent is still produced in "meilers."

In countries which do not utilise charcoal in the manufacture of iron, or at any rate only small quantities, the product is employed chiefly for domestic purposes. It is used for example as kitchen fuel, for heating bakers' ovens, in open braziers for heating living-rooms, and for heating laundry irons. It is also used for certain industrial purposes.

Charcoal is employed in smelting silver, copper, zinc, etc.; in forging brass; by coppersmiths, blacksmiths, goldsmiths, tinsmiths and plumbers; in iron foundries; and in many other trades where a hot fire without flame or smoke is required. Charcoal is still used for the manufacture of certain qualities of gunpowder, also for removing impurities from many chemical products such as carbon dioxide, ammonia, oxygen and alcohol.

Ground charcoal serves for the manufacture of smokeless briquettes which burn without flame, as a filtering medium, as moulders' blacking, in the manufacture of glass, and for other purposes.

Hence, charcoal forms an important, if not always easily saleable, article of commerce.

The more easily the charcoal can be sold, the higher its selling price and the lower the purchase-price of the wood, the better are the financial prospects of a wood-distillation factory.

Charcoal is characterised externally by retaining the form and structure of the wood from which it has been produced. The annual rings on the transverse section, the fibrous structure of the longitudinal section, and the shape of the bark are all clearly preserved and afford means of determining the origin of the product.

The following properties and behaviour are reliable indications that the quality of the charcoal is satisfactory: black and glistening appearance with a distinct bluish tinge; the production of a metallic note when struck on a hard object; freedom from taste and smell; adherence of small pieces to the tongue; a transverse face can be rubbed without soiling the fingers.

Charcoal of good quality must also be capable of easy ignition and must burn quietly without the production of smoke or flame.

A further peculiarity of charcoal is its *porosity*, which depends on the structure of the wood from which the product has been derived. Dense wood with narrow annual rings produces dense charcoal; rotten or porous wood gives rise to open, weak and easily friable charcoal. The cracks in the main body of the charcoal usually run in the direction of the transverse fibres and seldom in that of the longitudinal fibres. Charcoal from wood of small diameter, such as poles and branches, exhibits fewer cracks than charcoal from trunkwood.

Charcoal from rootwood contains the fewest cracks and pores.

The capacity of charcoal to adsorb gases and vapours, to extract certain substances from solution, to float on water and to ignite spontaneously is simply a function of its porosity.

Juon¹ determined the relative proportions of pores and solid substance and found :—

	Pores. Per cent by volume	Solid substance Per cent by volume.
Birch charcoal .	72·3	29·7
Spruce charcoal .	80·6	19·4
Silver fir charcoal .	84·7	15·3

Charcoal, after being cooled in absence of air, increases subsequently in weight owing to adsorption of gases and more especially water vapour. The extent of this increase differs for different kinds of charcoal and is also dependent on climatic conditions. After a certain time a state of equilibrium is reached, precisely as described in connection with the process of drying wood in the air. As a general rule—assuming that conditions of temperature are the same—equilibrium is reached in about three weeks ; the increase in weight then amounts to about 8 per cent, and about one-half of this increase is already attained after the charcoal has been stored for seventy-two hours.

In determining the yield of charcoal it is necessary to take into account this subsequent increase in weight, and therefore to weigh the product either directly after the cooling process (carried out in absence of air) or else only after it has lain for seventy-two hours in contact with air.

In order to arrive at the *selling weight* of charcoal it will be found sufficiently correct to add 7 per cent to the weight determined directly after cooling. At the same time, however, it is necessary to deduct the weight of the “smalls,” or “breeze,” which must be separated from the “stick charcoal”; this weight varies from 3 to 6 per cent of the total production of charcoal.

The residue of destructive distillation of wood is more or less rich in carbon according to the temperature at which the distillation process is broken off.

This is clearly evident from the experiments carried out by Violette (p. 44), and also from the more recent investigations of Juon (p. 40).

¹ Stahl und Eisen, 1904, 24, 1230.

It has been found by experience that for the production of charcoal which is not only quite black but possesses the remaining characteristic properties, the final temperature—measured in the interior of the carbonising apparatus—must be at least 370°C .

Charcoal produced at a temperature below 300°C ., appears red, or at least has a reddish tinge. This product is known as "red" or "foxy" charcoal; individual pieces are known as "brands," and are sorted out from the fully carbonised material.

At one time red charcoal was actually manufactured for gunpowder and for smelting purposes.

Under the influence of certain climatic conditions, such as extreme dryness, even a high grade, properly carbonised charcoal may assume a reddish tinge. Hence, colour alone is not always a safe standard for judging the quality of charcoal.

The speed of distillation has a considerable influence on the quantity of charcoal obtained.

The greater the rate of distillation, the higher is the initial temperature and the shorter is the interval between initial temperature and final temperature; the shorter the period of time corresponding to this interval of temperature, the lower is the yield of charcoal.

The experiments of Senff (p. 16) afford the best evidence on this point.

The charcoal "meilers," with their slow rate of carbonisation and long interval between initial and final temperatures, produce yields of charcoal which, in spite of admission of air and most primitive methods of operation, are equal to those obtained from ovens or retorts. No air, or only a regulated amount, is admitted into the latter, but on the other hand distillation is carried out more rapidly and the initial temperature is higher. It must be noted, however, that the weight of the charcoal produced in the "meilers" is considerably increased owing to quenching with water, which explains to a certain extent why the yields are apparently equal to those obtained from retorts.

Charcoal resulting from slow carbonisation is superior in quality; that is, richer in carbon. Although the carbon-content is regulated by the temperature at which carbonisation is completed, it also depends on whether the charcoal cools in the carbonising apparatus itself, or elsewhere. In the former

case the adsorption of hydrocarbons, as observed by Juon,¹ effects an increase of about 6 per cent in the carbon-content.

As regards yields of charcoal from different species of wood, it is impossible to give figures which hold good generally; the yield depends entirely on the quality of the wood available for carbonisation.

On page 52 a series of figures is given, representing yields obtained in practice; it should be noted that these figures were obtained immediately after the charcoal was cooled, and therefore before it had time to become saturated with water-vapour or gases.

Many published data lose practically all their value, owing to the fact that in stating the yield no information is given as to the elementary composition of the particular kind of charcoal in question and the quality of the original wood.

In this connection, reference may be made to the investigations of Senff, who determined the yields of charcoal from a large number of different species of wood. The results are tabulated on page 16.

In practice there are two methods of stating yields of charcoal:—

1. Percentage by weight.
2. Percentage by volume.

At the present day charcoal is mostly sold by weight, hence it should only be necessary to state the yields in percentages by weight. At the same time the yields in terms of volume possess a certain amount of interest, in view of the fact that charcoal is still sold by bulk-measure in some countries; for example, Sweden and the Urals.

According to von Berg² the meiler process gives the following yields of charcoal:—

	Per cent per volume.
Beech; smooth split billets, 150 mm. diam. upwards	64
Oak " " " "	66
Oak; branchwood, 50–150 mm. diam.	42
Spruce; split billets	78
Spruce; roots and stumps	68
Spruce; poles, 50–150 mm. diam.	58
Spruce (mixed)	72
Spruce; branchwood	46

¹ Loc. cit.

² "Anleitung zum Verkohlen des Holzes," 1860.

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These determinations were made with wood from the Harz.

Next in importance to the carbon-content of the charcoal (see below) is the weight of a bulk-measure.

Von Berg gives the following figures for the weights of 1 cu. metre of heaped charcoal produced in the Harz from various species of wood :—

1 cu. metre of charcoal from :—

	Kilos.
Beech ; split billets	weighs 185
Alder ; stout round and split billets	„ 137
Scotch pine ; split billets and root- and stumpwood	„ 166
„ „ round trunkwood billets	„ 136
„ „ branchwood	„ 106
Spruce ; split billets	„ 110
„ root- and stumpwood	„ 134
„ branchwood	„ 136

Juon,¹ on the other hand, obtained the following figures for charcoal obtained in the Urals from kilns of the Schwartz type :—

1 cu. metre of heaped charcoal from :—

	Kilos.
Birch	weighs 190
Spruce	148
Silver fir	131

In regard to the use of charcoal for technical furnace work the most important factors to consider are :—

Compressive strength.

The ease with which it is ignited.

Calorific value.

The comparative extent to which combustion takes place without the production of flame and smoke, and without giving rise to disintegration or emission of sparks.

The compressive strength of charcoal depends on the specific gravity of the individual pieces ; the calorific value depends on the carbon-content.

Again, in this connection, Juon furnishes exact data.

¹ Stahl und Eisen, 1904, 24, 1230.

He found that there was scarcely any difference in the specific gravity of the solid substance, exclusive of pores, derived from birch, spruce and silver fir charcoal; but on determining the specific gravity of charcoal cubes—that is, of the solid substance plus the pores—Juon obtained the following figures:—

	Specific gravity.
Birch charcoal, produced in kilns	. 0.40
Spruce " " " "	. 0.27
Silver fir " " " "	. 0.215

As a general rule, meiler charcoal is preferred to kiln charcoal, and kiln charcoal to retort charcoal.

It is difficult to decide how far this preference for one kind or the other is simply a matter of prejudice.

It is a fact, however, that the charcoal produced in these three different ways exhibits important differences, according to the temperature at which the carbonisation process is broken off and the nature of the cooling process. These differences apply not only to the carbon-content, but to the entire composition of the charcoal.

More recent data on the quantitative composition of charcoal derived from various sources may be found in the Swedish publication, "Om Kolning af Barrwed," by Hilding Bergström, Stockholm, 1904, from which the following average figures are taken:—

Source of Charcoal.	Carbon. Per cent.	Hydrogen. Per cent.	Oxygen + Nitrogen. Per cent.	Ash. Per cent.	Final tem- perature of carbonisa- tion. °C.
Meilers	90.36	2.74	5.72	1.1	Above 600
Kilns (with admis- sion of air)	84.18	3.32	11.72	0.78	500
Retorts (without ad- mission of air) . . .	81.15	4.24	13.64	0.97	350

This table clearly indicates the influence of the final temperature on the carbon-content of the charcoal, as already demonstrated by Violette (see page 44), who carried out the first investigations on this subject.

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This comparative summary also affords a plausible explanation of the preference shown for meiler charcoal for certain purposes.

Juon,¹ on the other hand, gives the following composition for different kinds of charcoal obtained from kilns, with admission of air :—

Charcoal from :	C. Per cent.	H. Per cent.	O + N. Per cent.	Ash. Per cent.	Calorific value in kilo-calories.
Birch . . .	75·04	3·49	19·83	0·90	6380
Spruce . . .	75·38	4·13	17·17	1·24	6500
Silver fir . .	73·41	3·45	20·63	1·26	6210

The carbon-content of charcoal is therefore the factor which controls the calorific value ; and the specific gravity of the individual pieces of charcoal is the factor which controls their strength or resistance to compression.

These points are clearly illustrated by the figures in the tables given below.

According to the Dulong formula : $h = 81C + 290(H - \frac{1}{8}O)$ kilo-calories, the calorific values for the three different kinds of charcoal possessing the composition shown in Bergström's table are as follows :—

	Calorific value.
Meiler charcoal	=7907 kilo-calories.
Kiln "	=7357 " "
Retort "	=7309 " "

Hence, the relationship between the calorific values of the three different kinds of charcoal may be expressed as :—

$$100 : 93 : 92.$$

In judging the value of charcoal for metallurgical purposes the most important factors to consider, apart from the ash-content—more especially the content of sulphur, silica and phosphorus—are the carbon-content, the specific gravity of the individual pieces, and the power of resistance in a diagonal direction in the cube.

Juon gives the following figures, showing the relationship

¹ Loc. cit.

between certain values for different kinds of charcoal, silver fir charcoal being taken = 1 :—

Ratios of :	Charcoal produced in kilns from :		
	Birch.	Spruce.	Silver Fir.
Carbon-content	1.02	1.03	1
Calorific value	1.02	1.05	1
Sp. gr. of the pore-free powder	1.06	1.01	1
Sp. gr. of individual pieces, including pores	1.88	1.25	1
Weight of 1 cu. metre of heaped pieces	1.45	1.13	1
Power of resistance (in a diagonal direction in the cube)	3.45	1.48	1

When charcoal is used as a reducing agent, the yield of metal corresponds with these values (especially the specific gravity of the individual pieces and their power of resistance). For birch charcoal and spruce charcoal, the yields of metal—referred to the same volume-unit—are as 1.5 : 1.17.

According to Juon the carbon in charcoal exists in three different forms :—

1. Solid carbon.
2. Volatile carbon.
3. Carbon produced by the adsorption of hydrocarbons, during the process of cooling in an atmosphere composed of those gases.

As regards the solid carbon it may be remarked that so far it has not been found possible, even by employing the highest attainable temperatures, to prepare charcoal which is entirely free from volatile matter, though the quantity present may be very small.

It is doubtful, therefore, whether charcoal contains any solid carbon in the elementary form. In view of its behaviour, it seems much more likely that even the most fully carbonised charcoal is really a compound of carbon and hydrogen.

It is therefore only possible to speak of "*volatile components*" of charcoal, if both the final temperature of carbonisation and the temperature to which the volatility refers are known.

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COMPOSITION OF SOFTWOOD CHARCOAL PRODUCED IN VARIOUS TYPES OF CARBONISING APPARATUS.

Carbonisation carried out in	Percentage composition.				Maximum temperature, at which carbonisation was finished. °C.
	Carbon.	Hydrogen	Oxygen+ Nitrogen.	Ash.	
MEILERS					
East Gothland, Sweden I.	90.6	2.9	5.6	0.9	} Above 600
„ II.	89.0	2.6	7.4	1.0	
„ III.	88.9	3.3	6.6	1.2	
Vernland, Sweden .	89.5	2.6	6.6	1.3	
Slabs carbonised at Iggesund, Sweden .	93.8	2.3	2.6	1.1	
Average .	90.36	2.74	5.72	1.1	

KILNS (WITH ADMISSION OF AIR)					
Boxholm kilns	82.0	3.5	14.0	0.5	350
Ljungberg kilns (page 136)	82.7	4.0	12.7	0.6	350
Ottelinska kilns (page 135)	87.0	2.9	9.0	1.1	520
	83.5	3.2	12.2	1.1	480
	85.7	3.0	10.7	0.6	500
Average	84.18	3.2	11.72	0.78	

RETORTS (WITHOUT ADMISSION OF AIR)					
Pipe ovens (page 138)	82.3	3.7	13.0	1.0	360
	80.8	4.1	14.2	0.9	360
	79.0	4.5	15.4	1.1	350
Carbo-ovens (page 143)	81.2	4.1	13.7	1.0	350
	80.9	4.4	13.7	1.0	350
	82.1	4.1	13.0	0.8	340
Gröndal retorts (page 157)	81.5	4.1	13.4	1.0	—
Average	81.15	4.24	13.64	0.97	

The following tables by Juon provide very clear information on this point :—

CHANGES IN WEIGHT ON HEATING VARIOUS KINDS OF
CHARCOAL IN ABSENCE OF AIR.

+ = percentage increase } in initial
- = percentage decrease } weights.

Charcoal (from kilns)	Temperatures in Centigrade degrees.							
	104°	155°	186°	284°	412°	500°	750°	1000°
Birch . .	-1.50	-1.08	-0.03	-2.81	-7.46	-22.16	-26.11	-31.84
Spruce . .	-1.08	-0.10	+0.73	-0.36	-3.11	-16.18	-22.30	-28.92
Silver fir . .	-1.03	-0.20	+0.86	-2.90	-8.35	-27.30	-31.16	-34.46

As will be seen from this table, the more important changes in charcoal which has been produced in kilns begin at about 350° C.

Hence it is possible, simply by heating the product in absence of air, to ascertain directly the temperature at which the carbonisation of any particular kind of charcoal has been finished.

CHAPTER IX

PREPARATION OF THE WOOD FOR CARBONISATION

THE main work of preparing the wood for carbonisation is already performed in the forest when the wood is being felled.

Felling is carried out in many different ways, for example, with the axe, with the saw alone, or with the axe and saw ; by uprooting the tree ; by cutting through the trunk with electrically heated wires ; by boring with electrically driven drills ; by means of portable steam-driven saws, etc.

Subsequent handling of the felled wood, sorting of the crop, removal of the wood to the loading station, stacking of wood at the loading station, and finally the different methods of transporting the wood from the forest to the factory, have already been considered in Chapter II.

The methods employed for carrying out these different operations are by no means uniform, but depend chiefly on the custom of the country and on local conditions and facilities.

In choosing the site for a factory, however, it is always necessary to bear in mind the feasibility of securing regular delivery of wood at a cheap rate, and dependent to the least possible extent on supplies of horses and carts, the state of the roads, the weather, etc.

Dimensions of Wood for Carbonisation.—The particular dimensions which must be given to the wood intended for carbonisation depend in the first place on the type of carbonising apparatus employed.

The period of distillation for carbonising apparatus designed for large charges extends over several days. In consequence, such apparatus is capable of dealing with wood of large dimensions, especially if there is partial admission of air as in certain types of kiln.

The American kilns (page 132), for example, completely carbonise trunks even of 400 mm. diameter. On the other

hand, the smaller types of carbonising apparatus, especially retorts, in which the period of distillation is shorter, must only be charged with wood of moderate dimensions, if it is desired to keep the distillation period within certain definite limits.

Wood which exceeds 300 mm. diameter (known as "double cleft") must therefore be split at least once, and wood of still greater diameter ("treble cleft") three or four times, for not only does the time required for distillation vary in proportion to the diameter of the wood, but the latter has also an influence on the yields. Thus, in an American factory which operated with horizontal car-retorts (page 149) of 25 cu. metres capacity, the author observed that maplewood of 150-200 mm. diameter required twenty hours for carbonisation compared with thirty-six hours for maplewood of 300 mm. diameter.

If possible, therefore, the diameter of split billets is not allowed to exceed 175 mm., the object being not only to ensure thorough carbonisation, but also to shorten the time required for drying the green wood and to regulate the strength and size of the charcoal. The greater the thickness of the wood, the longer is the period required for drying and the greater is the tendency of the charcoal to disintegrate during transport.

Wood-distillation factories which employ relatively small plant—for example, vertical retorts of 4-5 cu. metres capacity, or horizontal retorts of 1.5 cu. metres capacity—find it necessary to reduce the diameter of the wood still further and to work with split billets, round billets, etc., of 50-150 mm. diameter.

In France, particularly, large quantities of round billets and branchwood of small diameter are carbonised in vertical retorts, producing extremely durable charcoal which shows very little tendency to disintegrate.

As a general rule, the forest authorities are nearly always prepared to meet the needs and requirements of the local industry as far as possible, in regard both to thickness and length of the individual pieces of wood.

The purchaser finds it an advantage to buy large, smooth logs, as this means a considerable gain in the solid contents of the "forest" cu. metre. It is true that the large logs must be split later in the factory yard and that this operation entails certain costs, which have to be set against the gain in

the weight of wood. Nevertheless, the balance is in favour of the purchaser of this class of material.

If the seller and buyer are one and the same person, he will naturally take care that the felled wood is reduced to the correct dimensions while it is being split in the forest, especially in view of the fact that, owing to its bulk and unwieldy form, wood is difficult material to manipulate and double handling involves considerable cost.

After the wood has been delivered from the forest into the factory yard it must usually undergo further treatment in two respects :—

1. It must be cut to the required size for carbonisation, and all projecting portions which may interfere with the packing or prevent efficient utilisation of space in the carbonising apparatus must be removed.

2. It must be dried to the right degree.

The operations involved under (1) consist most frequently in hewing the billets so as to remove protruding branches, spikes, etc., also in splitting any "three-cleft" wood or other large-sized logs.

In carrying out these operations it is often the custom to chip away a certain amount of the bark and sometimes to remove the bark altogether, especially in the case of birch.

The peeled bark together with the other waste material can then be used as fuel.

The next operation consists in cutting the wood to the right size, if this has not been done already in the forest. Any billets which are too long should be cut to the proper length on a circular saw before being split.

In the forest, splitting is nearly always carried out with wooden or iron wedges operated by hand ; if further splitting is necessary in the factory, it should be done with a mechanically driven steel wedge, such as that shown in Fig. 3.

This machine consists of two iron pillars between which is an axle fitted with a crank or eccentric ; the latter, by means of a guide-rod, raises and lowers a steel wedge, the stroke of which can be regulated. The log is laid on two guide-ledges of suitable height, in such a position that the comparatively flat wedge, on descending, splits the billet in the direction of the fibres. One man using a machine of this type can split 60–70 cu. metres of wood, 0.5 metre in length, per day of ten hours without very great exertion, provided that the wood is

brought to the machine and removed from it by some other form of power.

These operations of cutting and splitting are carried out to a wide extent in the French factories, chiefly with the object of regulating the form and quality of the charcoal.

In a French factory which treats 120 cu. metres of split billets daily, three or four men are employed for moving the wood from the storage yard to the saws ; four men operate

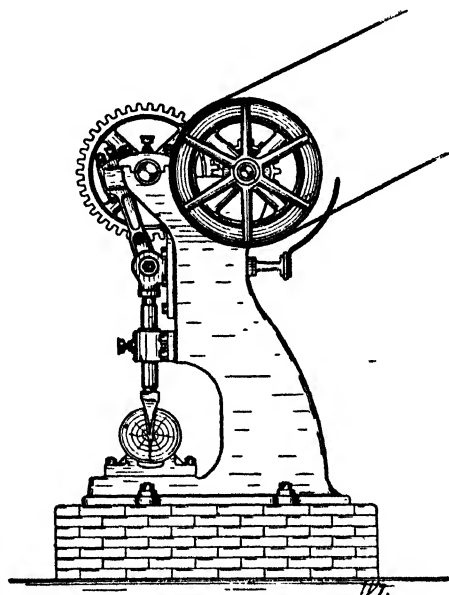


FIG. 3.—SPLITTING MACHINE.

two circular saws and two splitting machines ; and four men pack the wood into the retorts, which are usually of the vertical, portable type with a capacity of 4-5 cu. metres.

It will be obvious that this additional treatment of the wood must involve much manual labour, and, relatively, must be very expensive, especially if the cost of generating the power required for driving the circular saws and splitting machines—by no means a small amount—is also taken into account.

In countries where the rate of wages is high, for example, the United States, preliminary treatment of the wood in this

manner is impracticable. In these countries it is the custom to utilise, as far as possible, only those types of carbonising apparatus which, as regards the period of distillation and the quality of the charcoal produced, depend to a very small extent on the dimensions of the wood.

Examples of these types of apparatus are the large American kilns, the Swedish ovens and particularly the large retorts.

It may be said that the lengthy preparation of the wood before carbonisation, as described above, is practically confined to France and is carried out simply with a view to the production of the particular quality and form of charcoal demanded in that country. The price obtainable for the charcoal must then be sufficient to compensate for the considerable extra cost which such preparation entails.

Rootwood always requires a certain amount of extra preparation. It is very resistant to splitting, and in the forest, as a rule, it is only broken up sufficiently small by the use of explosives to permit of its bulk-measure being determined. The real disintegration is always carried out later in the factory itself, where it is dealt with first of all on the splitting machine, the sapwood and heartwood often being separated at the same time. If necessary it is cut up afterwards on the circular saw.

It is in the interest of every wood-distillation factory to avoid, if possible, all double handling and all additional treatment of the wood; in short, to reduce manipulation of the wood to a minimum. Failure in this direction always entails considerable increase in the cost of labour.

The most perfect example of simple manipulation was observed by the author in a large American factory which operated the type of kiln described on page 132. This factory treated 1000 cu. metres of wood daily and employed not more than fifty workmen, of which only thirty were engaged in dealing with the wood. The wood, in the form of logs and billets 200-400 mm. in diameter, was delivered every day from the forest in a train of twenty trucks. This train was run over a bridge which extended along the line of kilns, and the wood was discharged directly from the trucks into the kilns without any transshipment.

These figures, when compared with those given above for the cutting and splitting of 120 cu. metres of wood, demonstrate the enormous difference between simple and complicated manipulation in respect of the amount of labour required.

The smaller the carbonising chamber, the greater is the number of men required for a given output, the smaller must be the dimensions of the wood, and the greater the capital costs and above all the working costs.

Consequently, the tendency at the present day is to employ carbonising apparatus of large capacity, which is less dependent on the size of the wood used. The capital cost for large apparatus is proportionately lower than for small apparatus, and the cost of labour is greatly reduced.

Drying of the Wood.—The process of *pre-drying* which the wood must undergo before carbonisation is just as important as reduction of the wood to the correct dimensions.

As already stated on page 25, freshly felled wood contains 40–50 per cent of moisture.

It has also been shown that the moisture-content of wood intended for carbonisation is a very important factor.

Water possesses a very high heat of vaporisation. Since the water present in the wood must be evaporated in the first place during carbonisation, again in the subsequent distillation of the pyroligneous acid, and finally on evaporating the calcium acetate solution, it follows that if the moisture-content is excessive it must always lead to an increase in the fuel consumption of the factory.

It may be assumed that the total quantity of coal required for the distillation of 100 kilos. of air-dry wood containing 20 per cent of moisture (=80 kilos. of moisture-free wood) and for the subsequent treatment of the distillate, amounts to 25 kilos. For the preparation of 100 kilos. of wood containing 20 per cent of moisture, from wood containing 40 per cent of moisture.

$$\frac{100 \times 80}{60} = 133 \text{ kilos.}$$

of the latter must be dried, and $133 - 100 = 33$ kilos. of water must be expelled by evaporation. This will require $\frac{33}{7} = 4.71$ kilos. of coal, if the evaporative power of the coal is 7 : 1.

Hence, the amount of fuel required, when wood containing 40 per cent of moisture is used, must increase by at least

$$\frac{4.71 \times 100}{25} = 18.84 \text{ per cent}$$

compared with the amount required when the wood contains

only 20 per cent of moisture. This figure alone demonstrates the importance of keeping the moisture-content of the wood within normal limits ; but it is only one instance of the very prejudicial effect of abnormal moisture-content on the general operations and profits of a wood-distillation factory.

A further important consequence is considerable diminution in production. The area of heating surface with which the carbonising apparatus is provided allows only a certain definite amount of heat to reach the wood undergoing carbonisation, dependent on the temperature difference and the transmission coefficient between the heating agent and the surfaces transmitting the heat.

If, with a limited area of heating surface and a given difference of temperature, it becomes necessary to utilise a portion of the transmitted heat for evaporating water, it is obvious that the performance of the carbonising apparatus must diminish in proportion to the extent of this extra requirement.

In actual practice, high moisture-content is responsible for a considerable reduction in the output-capacity of a factory. For example, a factory operating horizontal retorts may be able to treat 45 metric tons of wood, containing 20 per cent of moisture, per day. If, on the other hand, wood containing 35-40 per cent of moisture is used—for example, wood which has been stored for two months after felling—the factory can only treat 30 metric tons per day.

Since the same general costs (wages, supervision, depreciation of the plant, interest on capital) are incurred for the treatment of 30 tons per day, *excessive moisture-content may easily bring about an increase of 50 per cent in the working costs.*

The detrimental effect of excess of moisture extends to the yields, especially the yield of acetate of lime.

A series of experiments, which the author was able to carry out owing to friendly interest on the part of the directorates of various wood-distillation factories, showed that the yield of acetate of lime, referred to 100 kilos. of moisture-free wood, was inversely proportional to the moisture-content of the wood.

The yield of charcoal, referred to the same unit, is less affected by high moisture-content, and the yield of methyl alcohol tends to increase.¹

¹ Cf. *Palmer and Cloukey*, Journ. Ind. Eng. Chem., 1918, 10, 262.

At the present day, however, acetate of lime is a very important product, and any reduction in yield represents a serious loss for the manufacturers, which is not compensated by a small increase in the yield of wood-naphtha.

In general it may be stated that the results of using wood containing excess of moisture are increase in the consumption of fuel, reduced output on the part of the factory, considerable increase in working costs, and reduction in the yield of acetate of lime.

The meaning of the term "*normal moisture-content*" must now be discussed.

It has been pointed out that absolutely dry wood is just as unsuitable for carbonisation as wood which contains an excess of moisture. If the wood is very dry, decomposition is no longer gradual; on the contrary, the products of distillation—especially if large carbonising apparatus is employed—are evolved spontaneously and often explosively, in such quantities that no condensing plant which can be installed at a reasonable cost is able to cope with them.

This sudden evolution of enormous quantities of gas and vapour is a source of danger and loss, which becomes all the greater as the capacity of the carbonising apparatus is increased.

We shall see later that these periods of violent evolution of gas and vapour cannot be entirely avoided, even when the moisture-content of the wood is normal.

In short, neither wet wood nor very dry wood forms suitable material for carbonisation. The most satisfactory quality lies between the two and is represented by wood containing 15–20 per cent of moisture.

Under the climatic conditions of Central Europe, wood containing 20 per cent of moisture is said to be "air-dry." A definition of "air-dryness" has already been given above, and it has also been mentioned that the moisture-content expressed by this term fluctuates according to the climatic conditions at the particular locality.

Air-dry wood containing 20 per cent of moisture can be described as of "normal moisture-content." As a general rule this degree of dryness is looked upon as sufficient.

Freshly cut wood from the forest contains 40–50 per cent of moisture, and for the reasons given above the first concern of every properly conducted wood-distillation factory is to

reduce the moisture-content of the green wood to 20 per cent, at the lowest possible cost.

This can only be accomplished by supplying the necessary amount of heat to dry the wood, and there are two ways in which the drying process may be carried out :—

1. *Slowly*, by means of air at atmospheric temperature.
2. *Rapidly*, by means of an artificial supply of heat and at increased temperature.

The first method involves storage of the wood for at least a year before it is fit for carbonisation ; for this reason, rapid artificial drying would at first sight appear to be preferable to the slow natural process.

Whether or not this view is correct is somewhat difficult to decide, but the fact remains that many expensive installations for artificial drying, after being erected with the fullest confidence as to results, have been pulled down again by their owners—who have gained experience but have lost capital—because artificial drying proved dearer than the natural process.

Only after a careful examination of the various factors which affect each individual case, is it possible to decide whether the natural or the artificial method should be chosen.

Figures always furnish the most reliable evidence and therefore an attempt will be made later to compare the costs of the two drying processes.

Natural Process of Drying Wood.—This is carried out by piling the wood—which must be properly trimmed and of the right dimensions—into stacks, either in an open field or, better still, on the factory ground. A layer of billets or slabs is laid down in the first place before building the stack, so as to prevent penetration of moisture from the ground ; and the stacks are so placed that the locally prevailing winds can find a passage through the interstices.

These stacks differ widely in form. In some cases the wood is piled in layers to a height of only a few metres, and gangways running lengthwise and crosswise are left between the separate stacks. In other cases no attempt is made to carry out this somewhat laborious process, but the stacks are constructed in the form of huge blocks which may be as much as 10–12 metres in height and breadth, and of any length, provided that the longitudinal face lies opposed to the direction of the prevailing winds.

Experience has shown that it is unnecessary to be too particular about the relative size of the individual stacks and the number of gangways.

All types of stack have one disadvantage in common, namely, that much labour is required to build them, especially if they are allowed to reach a great height.

In order to reduce the cost of stacking to a minimum, it has become necessary to use mechanical appliances, and the more efficient and reliable these appliances, the lower are the costs of drying by the natural process.

Transport of billetwood by mechanical means is not, however, a very simple matter, since the continuously operating devices employed for moving large masses of material, such as conveyor belts, overhead cableways and elevators, can only be applied to the irregular blocks of wood after undergoing suitable modification.

Transport of wood in a horizontal direction is practically always carried out in trucks. In small factories these trucks are moved by hand; factories of medium size make use of horses for the purpose, and only the largest factories employ locomotives or electric power.

Trucks, conveyer-belts, and elevators are always loaded by hand, since no automatically operating loading-machines capable of dealing with such irregular material have yet been introduced.

In building the stacks, the wood is usually lifted by hand, in spite of the fact that this method is very laborious and that machines specially designed for the purpose and both cheap and reliable may now be obtained.

Two distinct types of machine are in use, viz. :—

1. Stationary elevators.
2. Travelling hoists.

Stationary elevators are more suitable when the lifting operations are only carried out at one particular point. These elevators are fitted with lifting-arms on which one or more logs are laid by hand. As each pair of lifting-arms arrives at the top, the load is removed, again by hand. Thus the elevator operates quite continuously and is suitable for charging stationary carbonising apparatus such as large ovens.

The stationary elevator is less suitable for stacking wood, as it only operates in one direction. The best form of machine

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for this purpose is one which can be moved along the face of the stack as the latter is being built. A machine of this type is shown in Fig. 4.

The frame of the machine is fitted with wheels which run

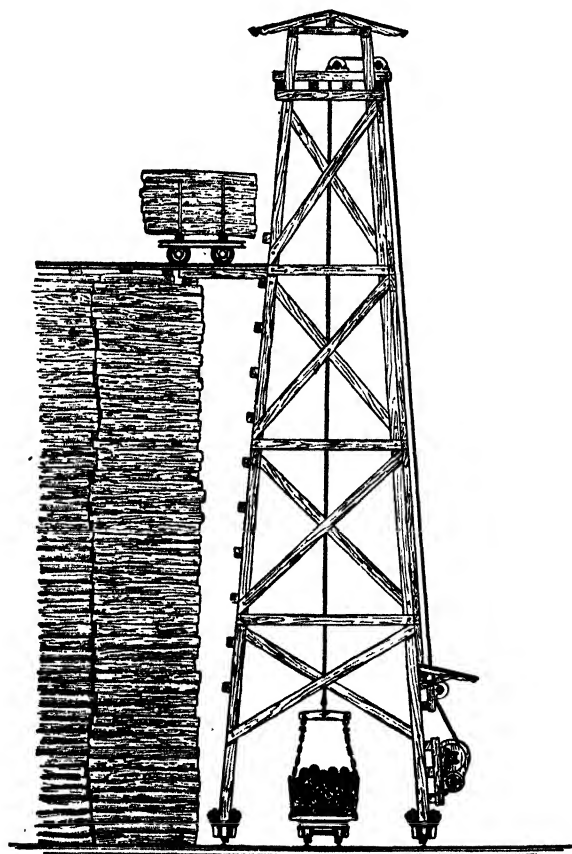


FIG. 4.—TRAVELLING HOIST

on a rail-track laid down along the front of the wood-stack. On the side of the frame is a winch operated either by hand or by electric motor. The winch winds a cable which passes over pulleys at the top of the machine and lifts the load of wood to the requisite height. The load is received in cars of

suitable size running on a temporary narrow-gauge track, which can be laid in any position on the top of the stack. The load is then dispatched to any desired point and there discharged.

This exceedingly practical device was first seen by the author at a French factory. The machine can be moved without difficulty in a horizontal direction along the stack and used to hoist the wood, either in bundles bound round with a chain, or in trucks which by means of the rail-track on top of the stack can traverse the latter in any direction.

This arrangement can, of course, be modified in numerous different ways, but there is no need here to deal with all the possible variations which local conditions may render necessary.

By operating in the manner described above, it is possible to build large stacks of wood well and efficiently.

In breaking down the stacks, the hoist is used until the surface of the part undergoing demolition has acquired the form of an inclined plane. The machine is then removed and the wood is allowed to fall to the ground simply by force of gravity, assisted if necessary by means of long iron bars.

To become "air-dry" the wood must remain in the stacks for at least one to two years. The period varies according to the kind of wood, its thickness, and whether it consists of split billets, or round billets still covered with bark; further, according to the temperature of the atmosphere, the direction and amount of wind, and the number of bright and dry or cloudy and damp days.

The costs of the natural drying process may be calculated from the following data :—

- (a) Interest on the value of the ground occupied by the stacks.
- (b) Interest on the capital invested in the stacked wood.
- (c) Cost of labour for building and breaking down the stacks.
- (d) Working costs and depreciation of the lifting machine.

We will assume that these costs refer to a factory which carbonises 100 cu. metres of air-dry wood (40 metric tons) per day; that the period required for drying is only one year; and that the price of the wood is 5s. per cu. metre of air-dry wood at the factory.

- (a) 100 cu. metres of wood per day represent a total amount

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of 36,000 cu. metres which, if stacked to a height of 10 metres, will cover an area of about 5000 square metres, including cartways, etc.

Assuming that the price of the ground is 2s. per sq. metre, the total area represents a taxable value of 10,000s. (£500), which, at $4\frac{1}{2}$ per cent interest, entails an annual charge of 450s. (£22 10s.), or $\frac{450}{36,000} = 0.0125$ s. per 1 cu. metre of wood.

(b) At a purchase price of 5s. per cu. metre 36,000 cu. metres of wood treated yearly represent a capital outlay of $36,000 \times 5 = 180,000$ s. (£9000), which, at $4\frac{1}{2}$ per cent interest, entails a charge of 8100s. or $\frac{8100}{36,000} = 0.225$ s. per 1 cu. metre.

(c) If we reckon that five men are required for stacking 100 cu. metres of wood daily (twelve hours), and that the wage for each man per twelve-hour shift is 3s., then the cost of stacking for one year =

$360 \times 15 = 5400$ s. (£270), or $\frac{360 \times 15}{36,000} = 0.15$ s. per cu. metre.

(d) In addition there is a charge of 0.05s. per cu. metre for the operating costs and depreciation of the lifting machine.

In the above conditions, which will vary, of course, for different cases, the total costs of the natural drying process, when the latter extends over a period of one year, amount to :—

	Shillings.
Interest on value of ground	0.012
Interest on capital invested in the wood, if purchased for cash	0.225
Wages	0.150
Operating costs, etc., of lifting machine	0.050
Total per 1 cu. metre of wood	0.437

Artificial Process of Drying Wood.—*The artificial process of drying wood* may now be considered.

One hundred kilos. of air-dry wood containing 20 per cent of moisture are obtained by drying 133 kilos. of wood containing 40 per cent of moisture, and 33 kilos. of water must be evaporated during the process.

Hence, to obtain 1 cu. metre (400 kilos.) of air-dry wood

it is necessary to dry 532 kilos. of wet wood, and the amount of water to be evaporated is 132 kilos.

Artificial drying of wood is carried out by allowing hot furnace gases or hot air to act directly on the wood.

The first attempts to dry wood were made with the hot gases from the retort furnace before they passed into the chimney. The gases were drawn off by means of a fan and forced through chambers into which cars containing the wood had previously been introduced.

An objection to this method was the great danger of fire, as a result of bringing furnace gases, at a temperature of over 300° C. and still containing a relatively high proportion of oxygen, into direct contact with the wood.

Wood is an extremely difficult material to dry, especially in pieces of relatively large diameter such as split and round billets. With wood of this size containing 40 per cent of moisture there is not much danger of fire as long as no small fine fragments are present. Splinters, thin twigs, etc., dry very quickly under the influence of the hot furnace gases and rapidly become ignited. Experience has shown that owing to the danger of fire it is impracticable to dry wood by direct action of hot furnace gases. The temperature at which drying is carried out must be maintained at such a degree that ignition of the wood cannot be brought about as a result of small particles catching fire in the first place.

Attempts have been made to avoid the danger of fire by conveying the heat of the furnace gases indirectly to the wood, but even under these conditions it is found that the danger is not prevented but only reduced.

A serious disadvantage attaching to all drying methods which depend on the direct or indirect action of the furnace gases before entering the chimney is the possible effect on the chimney draught. This suffers if the gases are cooled beyond a certain point and may even be cut off altogether, especially in bad weather.

In all cases where the drying process is carried out on these lines, the draught must be created artificially by means of a fan. Fans, however, consume a considerable amount of power, and power is always expensive, as will be illustrated later in dealing with costs.

The process of drying the wood must therefore be carried out at such a temperature that ignition, even of small splinters,

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is impossible. To fulfil this condition the temperature must not exceed about 150°C .

There is a further reason, based on purely practical considerations, against the use of high temperatures for the drying process.

If the billets are laid parallel to one another—according to the usual practice—the time required for drying is very lengthy. It can be reduced by arranging the layers in criss-cross fashion, but this necessitates unloading the wood after the drying process is completed, and rearranging it in parallel layers in the carbonising apparatus or retort-cars. These operations involve considerable handling, but to handle wood at 150°C . is not a very feasible proposition.

If the wood is allowed to cool it takes up moisture again very rapidly from the air. Hence there is no advantage in drying at a higher temperature than that at which the wood can be handled.

Drying at high temperatures also causes cracking of the wood, and as a consequence the production of inferior charcoal.

In short, wood can only be dried satisfactorily at a relatively low temperature, and naturally the time required by the process is lengthened accordingly.

In practice a temperature of 100°C . inside the drying chamber has proved suitable. The actual process consists in passing air which has been preheated to 100°C ., or possibly somewhat higher, through the chamber.

In order to compare the costs of artificial drying with those of the natural process, it is necessary in the first place to determine the amount of heat which must be supplied for carrying out the artificial process.

Assuming that the walls of the drying chamber are already heated up to the working temperature, the total expenditure of heat is made up of the following amounts :—

1. Heat required to raise the temperature of—

- (a) the wood-substance,
- (b) the moisture present in the wood,
- (c) the cars containing the wood,

to 100°C .

2. Heat required to expel the moisture from the wood by evaporation.

3. Heat carried away by the air passing out of the drying chamber.

4. Heat required to generate power for driving the fan.

5. Loss of heat by radiation from the walls of the drying chamber.

The following calculations refer to 532 kilos. of wet wood containing 40 per cent of moisture, which will produce 400 kilos.—1 stacked cu. metre—of air-dry wood containing 20 per cent of moisture.

1. 532 kilos. of wet wood (40 per cent of moisture) contain :—
 320 kilos. of moisture-free wood (specific heat = 0.6).
 212 „ „ water.

Of this weight of water, 132 kilos. are to be evaporated.

The wood is to be dried on cars which have a capacity of 6 cu. metres and weigh 1000 kilos. Hence, 532 kilos. of wood correspond to $\frac{1000}{6} = 166$ kilos. of iron of which the cars are composed.

To raise the temperature of these materials to 100° C. the following amounts of heat must be supplied, respectively :—

	Kilo-calories.
(a) 320(100—15) × 0.6	= 16,320
(b) 212(100—15) × 1.0	= 18,020
(c) 166(100—15) × 0.114	= 1,600
Total	= 35,940

2. The evaporation of 132 kilos. of water requires
 132 × 530 = 69,960 kilo-calories.

3. As already mentioned, the process of drying is carried out by heating atmospheric air to at least 100° C. in some form of preheater, by means of any suitable source of heat, and conducting it over the wood. The air gives up heat to the wood, whereby the drying is effected, and then passes out of the drying chamber.

The temperature and relative humidity of the outflowing air determine the amount of heat carried away from the chamber.

Experience has shown that air which enters the chamber at a temperature of 100–110° C. leaves the chamber at a temperature of not less than 60° C., and with a relative humidity of 25.

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By referring to the formulæ which are given in every textbook of physics it will be found that 1 cu. metre of air under the above conditions contains :—

1.004 kilos. of dry air.
0.0328 „ „ water vapour.

Assuming that the air enters the preheater at a temperature of 20° C. and with a relative humidity of 75, 1.004 kilos. of dry air are equivalent to 0.848 cu. metre of moist air containing 0.011 kilo. of water vapour.

Hence, each cubic metre of air leaving the drying chamber at a temperature of 60° C. and with a relative humidity of 25 carries with it 0.0328 kilo. of water vapour, of which 0.011 kilo. have been introduced by the air entering the chamber.

In order to expel $0.0328 - 0.011 = 0.0218$ kilo. of water by evaporation from the wood, it is necessary, therefore, to remove 1.004 kilos. of air at 60° C. and 0.0328 kilo. of water vapour from the drying chamber.

By means of these figures we can calculate the corresponding values for 132 kilos. of water, equivalent to 532 kilos. of wet wood, thus,

$$\begin{aligned} 0.0218 : 1.004 &= 132 : x \\ x &= 6080 \text{ kilos. of air.} \\ 0.0218 : 0.0328 &= 132 : x \\ x &= \text{approx. 200 kilos. of water vapour.} \end{aligned}$$

Taking the specific heat of air = 0.2375, and of water vapour (superheated) = 0.475, the amount of heat removed from the drying chamber, during the evaporation of 132 kilos. of water from 532 kilos. of wet wood, is the following :—

	Kilo- calories.
$6080(60-20) \times 0.2375$	$= 57,760$
$200(60-20) \times 0.475$	$= 3,800$
Total	<u>61,560</u>

4. The amount of heat required to generate power for driving the fan, without which uniform operation is impossible, may be calculated as follows :—

1 cu. metre of dry wood requires approx. 6080 kilos. of dry
 $\text{air} = \frac{6080}{1.184} = 5135$ cu. metres of air at 20° C., with a
 relative humidity of 75.

Hence, a drying installation which is capable of treating 100 cu. metres requires $\frac{5135 \times 100}{24} = 21,400$ cu. metres of air per hour of a 24-hour period of drying, or $\frac{21,400}{3,600} = \text{approx. } 6$ cu. metres per second.

According to the formula

$$N = \frac{Q \times h}{75 \times r}$$

where Q = volume of air per second,

h = pressure of air in millimetres of water,

r = efficiency = 0.4,

the power N required to drive the fan

$$= \frac{6 \times 200}{75 \times 0.4} = \frac{1200}{30} = 40 \text{ horse power,}$$

which for 24 hours' operation requires $40 \times 24 \times 16 = 15,360$ kilos. of steam.

Of this amount of steam, however, at least 70 per cent can be utilised, after it leaves the exhaust of the engine which drives the fan, for preheating the air. The net amount of steam consumed is therefore only :—

$$15,360 - \frac{70 \times 15,360}{100} = 4608 \text{ kilos.} = \frac{4608}{7} = 659 \text{ kilos. of coal,}$$

equivalent to $659 \times 7000 = 4,613,000$ kilo-calories for the generation of power per 100 cu. metres, or 46,130 kilo-calories per 1 cu. metre.

5. In practice, it has been found that a drying period of 72 hours is necessary for the reduction of the moisture-content of billets with a diameter of 150 mm., from 40 per cent to 20 per cent, at a working temperature of 100° C. The drying plant must therefore be of sufficient capacity to contain three times the quantity of wood which is carbonised daily. Hence, theoretically, for every cubic metre of wood carbonised, 3 cu. metres of drying-chamber space must be provided. Owing to the use of cars to contain the wood, only about 60 per cent of the available drying space is actually utilised, with the result that, in practice, 1 cu. metre of wood requires 5 cu. metres of drying-chamber space; for example, a space 2 metres high, 2 metres wide and 1.25 metres long. Leaving the end walls completely out of consideration, since they are

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common to a large mass of wood, 7.5 sq. metres of brickwork per 1 cu. metre of wood remain.

If the mean atmospheric temperature is 17° C., the difference in temperature between the inside of the chamber (100° C.) and the atmosphere is 83° C.

Since 1 sq. metre of brickwork, 380 mm. thick, loses about 100 kilo-calories per hour, it follows that the amount of heat lost by radiation from 7.5 sq. metres of brickwork, per 24 hours and 1 cu. metre of dried wood =

$$7.5 \times 100 \times 24 = 18,000 \text{ kilo-calories.}$$

The *total heat* required for drying 532 kilos. of wood, containing 40 per cent of moisture, to 400 kilos. (= 1 cu. metre) containing 20 per cent of moisture, by the artificial process, is made up as follows :—

1. Heat required to raise the temperature of	
(a) 532 kilos. of wet wood,	
(b) the moisture present in the wood,	
(c) the cars containing the wood,	Kilo.-
to 100° C	calories.
	= 35,940
2. Heat required to evaporate 132 kilos. of water	
from the wood	= 69,960
3. Heat removed by outflowing air	= 61,560
4. Heat required to generate power for driving	
the fan	= 46,130
5. Heat lost by radiation from the brickwork of	
the drying chamber	= 18,000
	Total = 231,590

The air entering the drying chamber must therefore supply 231,590 kilo-calories per 1 cu. metre of dried wood. Assuming that 75 per cent of the theoretical heating power of coal is utilised (5250 kilo-calories per kilo.) then

$$\frac{231,590}{5250} = 44.1 \text{ kilos. of coal.}$$

At a price of 12s. per metric ton for coal, the cost of *fuel* alone per 1 cu. metre of dried wood = $\frac{44.1 \times 12}{1000} = 0.53s.$

This figure by no means covers the cost of artificial drying.

The drying installation, which includes drying chambers, wood-cars, plant for preheating the air, fan, steam engine for driving the fan and moving the cars, costs at least £30 per

unit of capacity (1 cu. metre of dried wood). Reckoning the charge for *depreciation* at 10 per cent per annum this figure represents 0.17s. per cu. metre of dried wood. Adding *wages*, reckoned at 0.15s., the charges per cu. metre work out as follows :—

	Shilling.
Fuel	0.53 (coal at 12s. per metric ton).
Depreciation of plant	0.17
Wages	0.15
Total	0.85

The following table shows the costs of drying by natural and artificial processes respectively, per 1 cu. metre of dried wood :—

	Natural drying. Shillings.	Artificial drying. Shillings.
Interest on value of ground	0.012	—
Depreciation charge for drying plant	—	0.17
4½ per cent interest on capital invested in the stock of wood	0.225	—
Fuel	—	0.53
Operating costs, etc., of lifting machine	0.050	—
Wages	0.150	0.15
Total	0.437	0.85

This comparison indicates quite clearly the extent to which artificial drying is likely to be successful from the financial point of view, under the conditions stated above. It also explains why, in practice, so many drying installations, after operating for a certain time, have proved to be uneconomical, and have been closed down.

It is possible, of course, to bring about a very considerable reduction in the cost of fuel (0.53s.) by making use of the numerous sources of waste heat, which are always to be found in every wood-distillation factory, for the purpose of pre-heating the air.

In this connection it will be of interest to examine the prospects of utilising the following sources of waste heat :—

1. Flue Gases from the Boiler and Retort Furnaces.—

For every cu. metre of wood carbonised, 100 kilos. of coal are burnt under the boilers and retorts, producing $100 \times 21 = 2100$ kilos. of flue gases, which leave the furnaces at an average

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temperature of 300° C. (boilers, 250° C. ; retorts, 350° C.). Since these gases can be cooled to 250° C. without injuring the chimney draught it should be possible to utilise

$2100(300-250) \times 0.23 = 24,150$ kilo-calories
without much difficulty.

2. Charcoal at a Temperature of 450° C.—Utilisation of the heat contained in the freshly discharged charcoal would prove more difficult. Assuming a yield of 100 kilos. of charcoal from 1 cu. metre (=400 kilos.) of wood, the amount of heat available from this source = $100 \times 450 \times 0.2$ (sp. ht. of charcoal) = 9000 kilo-calories.

3. Hot Gases and Vapours leaving the Carbonising Apparatus.—It would be still more difficult to make use of the latent heat contained in the gases and vapours passing from the retorts, etc., into the condensers.

Assuming that the mean exit temperature of the volatile products is 300° C., 1 cu. metre of wood (400 kilos.) will furnish :—

	Kilo-calories.
200 kilos. of pyroligneous acid at 300° C. (reckoned as superheated water vapour) ;	
$200 [630 - 20 + (300 - 100) \times 0.475]$	= 141,000
100 kilos. of wood-gas (reckoned as air) at 300° C. ;	
$100 \times (300 - 20) \times 0.23$	= 6,440
	<hr/>
Total	= 147,440

This amount of heat, however, is only available if the distillate is cooled by means of *air condensers*, around which the air to be used for the drying process is *artificially* circulated. Since these condensers must be made of copper and must have a much greater surface than water-cooled condensers, it is easy to show by calculation that the gain in the one direction is almost completely neutralised by the much higher charge for depreciation which the use of air-condensing plant involves.

Under the most favourable conditions the following amounts of waste heat are available from the above-mentioned sources :

	Kilo-calories.
Furnace gases . . . :	24,150
Charcoal	9,000
Volatile distillation products	147,440
Total	180,590

Of this amount, however, only about one-sixth is really free of cost.

Hence, under normal conditions artificial drying of wood by means of the waste heat from various sources in a wood-distillation factory is impracticable.

Although the most elaborate methods of conserving heat may be employed, the saving in fuel is always counter-balanced by increased charges for depreciation, and other costs.

Even if waste heat could be utilised without any increase in cost, or if absolutely free fuel were available, which is very rarely the case in practice, it is only seldom that artificial drying would offer any advantage. The above table shows that the amount represented by the interest at $4\frac{1}{2}$ per cent on capital invested in a stock of wood sufficient for a year's production, is not much higher than the 10 per cent charge for depreciation on the capital cost of an installation for artificial drying.

Comparison of these two figures alone should be sufficient to settle the question as to the relative advantages of natural drying over a period of one year, and artificial drying over a period of three days.

It is possible of course that the original conditions may be different; for example, it may be necessary to extend the period of natural drying to $1\frac{1}{2}$ —2 years. In this case the prospects of utilising the artificial process with satisfactory results are naturally better.

The above calculations are based on actual practical data, as well as on the physical laws governing the processes under discussion. By utilising this information in discussing the practicability of a proposed drying plant, it should be possible to avoid the experience which has been so frequent in the past—namely, the necessity of closing down an expensive installation owing to its failure to effect any economy.

It is possible, however, to save a certain amount of fuel by preheating the air-dry wood before carbonisation. The amount of heat required to preheat 1 cu. metre of air-dry wood to 100°C . is about 25,000 kilo-calories = $\frac{25,000}{5,000} = 5$ kilos. of coal (efficiency = 70 per cent). The amount of coal required, in addition to the non-condensable gases, for carbonising 1 cu. metre of wood = 20–30 kilos.; hence, by preheating the

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wood to 100°C., not only would 20 per cent of the fuel for the retort furnaces be saved, but at the same time the working capacity of the plant would be increased.

The simplest method of preheating consists in allowing the flue gases from the retort fires, before entering the chimney, to circulate round chambers which contain the wood.

Direct action of the flue gases on the wood is not permissible owing to the danger of fire (see above).

We can ascertain by calculation whether the available heat of the flue gases is sufficient for this purpose.

Assuming that the gases are supplied to the chambers containing the wood at a temperature of about 350°C. :—

1 cu. metre of carbon dioxide at 15°C. and 1 atm. (1 cu. metre CO_2 = 1.862 kilos.) contains 0.508 kilo. of carbon; hence, 6.5 per cent CO_2 in the flue gases corresponds to $0.065 \times 0.508 = 0.033$ kilo. of carbon per cu. metre. 1 kilo. of coal containing 76 per cent of carbon will therefore produce $\frac{0.760}{0.033} = 23.03$ cu. metres of flue gases at 15°C. and 1 atm.; and 25 kilos. of coal will produce 575.75 cu. metres.

The non-condensable gases, which are burnt under the retort at the same time, amount to 60 cu. metres per 1 cu. metre of wood carbonised; 1 cu. metre of these gases on combustion (see page 56) produces 2.838 cu. metres of flue gases at 15°C. and 1 atm. Hence, 60 cu. metres produce $60 \times 2.838 = 170$ cu. metres of flue gases.

Assuming that the normal consumption of fuel amounts to 25 kilos. of coal per 1 cu. metre of air-dry wood (400 kilos.), that the flue gases enter the drying plant at a temperature of 350°C., and that the specific heat of the gases = 0.314 per cu. metre, it follows that the total amount of heat which can be supplied free of cost *without injuring the chimney draught* is :—

$$(575.75 + 170) \times (350 - 250) \times 0.314 = 23,416 \text{ kilo-calories.}$$

Since about 25,000 kilo-calories are required for *preheating* air-dry wood, it is obvious that *with a normal consumption of fuel* the flue gases from the retort furnaces can never reduce the moisture-content of wood containing more than 20 per cent of moisture. At the most the gases are able to preheat the wood to a certain degree.

The preheating process is really only free of cost if it involves no extra handling of the wood.

Where movable carbonising apparatus is employed, such as vertical retorts which are charged with the wood before being placed in the furnace, or where retort-cars (page 150) or baskets (page 140) are used, no special transport or re-arrangement of the wood is necessary. In these cases the result of the preheating process is not only a saving of fuel, but an increase in the working capacity of the plant.

The process is particularly easy to carry out in those factories which employ car-retorts. In front of the retort a brickwork chamber may be built, around which the flue gases from the retort furnaces are circulated before passing into the chimney. The cars, loaded with wood and ready for the next retort run, are placed in the chamber and allowed to remain there during one operating period of the retort. If suitable dampers are provided, there is no difficulty in inducing a current of air, which can be regulated at will, to pass through the chamber by natural draught.

In patent-literature and other publications, the process of "predrying" the wood by means of the waste gases from the furnaces of the carbonising apparatus is frequently described as a very marked improvement in connection with the process of wood-distillation.

By utilising the heat of the flue gases, so far as that is possible without danger to the chimney draught, together with the heat contained in the charcoal, the highest possible saving which can be effected amounts to 33,000 kilo-calories per cu. metre of wood. This represents a saving of about 4.7 per cent in the total consumption of fuel, if we assume that the normal amount of coal (at 7000 kilo-cals.) required for the whole process, including the production of wood-naphtha and acetate of lime, is 100 kilos. (=700,000 kilo-calories) per 1 cu. metre of wood.

These figures demonstrate very clearly that the utilisation of waste heat in this manner, though so very widely advocated, is only of small significance compared with the total fuel requirements of a wood-distillation factory.

CHAPTER X

THE CARBONISING APPARATUS; STRUCTURAL DETAILS

1. General.—The external phenomena which may be observed during the carbonisation of wood have already been discussed in Chapter III.

It was shown that the process could be divided into four different phases :—

1. The period in which the moisture present in the wood is evaporated as a result of supplying heat from an external source. Practically no gas is formed, and the average temperature during the period is about 170°C .

2. The period in which the temperature rises from about 170° to 270°C . as a result of external heating. Pyroligneous acid vapour, a little tarry vapour, and gas consisting almost entirely of carbon monoxide and dioxide are evolved.

3. The exothermic, or "auto-carbonisation" period which sets in when the wood has reached a temperature of 270° – 280°C . During this period no external application of heat is necessary, the non-condensable gas contains a relatively large proportion of hydrocarbons, and the main bulk of the tar and wood-naphtha is produced.

4. The period in which the charcoal becomes completely carbonised. Hydrocarbons are adsorbed by the charcoal, and condense to form solid compounds.

In order to initiate the first phase and to carry the process as far as the completion of the second phase, it is essential to heat the wood ; hence, every carbonising apparatus must be provided with an easily regulated arrangement for supplying heat.

If it be possible to supply heat so uniformly that every single piece of wood in the carbonising apparatus reaches the same temperature at the same time, then at first only water

is given off by the wood. As long as the wood still contains water, the temperature in the apparatus remains comparatively low and does not reach the point at which the actual process of carbonisation sets in.

Only after the main bulk of the moisture has been evaporated does the temperature rise, and simultaneously, the actual decomposition of the wood begin. When the wood reaches a temperature of 280°C . decomposition becomes particularly intense, and volatile products—consisting of gas rich in hydrocarbons, pyroligneous acid vapour, and tarry vapour—are evolved in considerable quantities, even if the supply of heat is cut off completely.

In designing carbonising apparatus, and particularly condensing plant, it is obvious that the occurrence of this violent reaction must be kept in view.

After the reaction has ceased, the process of carbonisation again enters a calmer phase in which the rate of flow of the distillate is more uniform, though the flow of gas does not diminish.

In actual practice, however, the transition of the dried wood into charcoal and volatile products takes place more or less gradually, owing to the fact that when large-scale carbonising apparatus is employed, it is impossible as a rule to conduct the process in such a regular manner that the *whole* charge of wood is first deprived of its moisture and then enters the phase of active decomposition.

The particular phase of the process which each individual piece of wood has reached will vary according to the distance which separates it from the source of heat and whether or not it lies in the main path of the flow of gas. The longer it is possible to retain a certain amount of wood, still containing moisture, uniformly distributed throughout the apparatus, the less violent is the course of the process, since the moisture-content of the charge is the controlling factor in regard to the intensity with which the actual process of carbonisation sets in.

Every carbonising apparatus may be divided into three main sections :—

1. The container for receiving the charge of wood, together with the arrangements for charging and discharging.
2. The arrangements for supplying heat and for conveying the flue gases from the apparatus.

3. The arrangements for conveying the volatile products of distillation from the apparatus.

The design of each of these sections is capable of very wide modification; hence it is possible to construct carbonising apparatus of many different types, as will be seen by consulting technical and patent literature, in which an immense number is described.

In this book no useful purpose will be served by describing all the various forms of apparatus which have been suggested. It is intended to deal only with those types which allow the by-products to be recovered, and only with such representatives as the author has actually seen in practical operation in the course of his travels in Europe and America, or of which he possesses authentic information. By observing this principle the number of types becomes considerably reduced. An attempt will be made later to draw up a scheme of classification for the different forms of carbonising apparatus in use at the present day; first of all, the three main sections of the apparatus must be considered from a general point of view.

2. Building Materials.—The most prominent feature of every carbonising apparatus is the container, and the first matters to decide are the most suitable building materials and dimensions for the container.

Only two kinds of building material come into consideration, viz. *firebrick* and *steel*. Sometimes, though only seldom, these materials are combined by erecting a steel structure and lining it with brickwork.

If firebrick alone is used for constructing the container, it is impossible to prevent the occurrence of fissures and cracks which cause more or less serious loss of volatile distillation products. For this reason, firebrick, though relatively cheap, is only used when the manufacture of charcoal is the main object and the recovery of the volatile products is of secondary importance. Moreover, the use of brickwork makes it practically impossible to supply heat to the charge *through* the walls of the container, and it becomes necessary to employ furnace gases as direct carriers of heat, or, preferably, to provide an internal heating system constructed of iron, through which the furnace gases can be circulated without coming into direct contact with the wood.

With this type of brickwork apparatus it is certainly

possible to avoid admission of air directly to the wood and at the same time to prevent partial combustion of the by-products. Like all similar forms of apparatus, however, it suffers from the disadvantage that cracks and fissures are formed in the brickwork shell, with loss of volatile products as a result. This loss can be minimised by applying suction, as in the American kilns (p. 132), but air is then drawn in through the cracks, and loss arises owing to combustion of the wood, charcoal, or volatile products.

In all circumstances, therefore, the use of brickwork for the shell of the container entails loss of products, and for this reason all modern containers—even those of the largest dimensions (400 cu. metres capacity)—are constructed only of steel, or at any rate the latter material is used as an outer covering for the brickwork.

Steel proves a most serviceable material for the construction of carbonising apparatus, provided that only plates of superior quality are selected and the masonry setting is so constructed that no fine-pointed flames can impinge on the plates; that uniform heating can take place with the smallest possible differences of temperature; and that the apparatus can expand unhindered.

As frequently emphasised above, an internal temperature of 400° C. is sufficient for the carbonisation of the wood. In order to ensure that a certain definite quantity of heat shall pass from the outside of the apparatus to the inside, certain differences in temperature must exist between the exterior of the steel shell, the shell itself, and the interior of the apparatus. The larger the heating surface of the apparatus, the smaller need these differences in temperature be. Hence, by regulating the area of the heating surface, it is possible to work with a higher or lower external temperature accordingly.

With the object of sparing the plates, the precaution is taken, in designing carbonising apparatus, of providing the largest possible heating surfaces. In these conditions, the temperature of the furnace gases supplying the heat and of the plates transmitting the heat to the interior of the apparatus need only be comparatively low. If, on the other hand, the heating surface is small, the temperature of the plates transmitting the heat must be relatively high for a given performance on the part of the apparatus. In these conditions it also follows that the volatile products leaving the apparatus

must undergo secondary decomposition involving loss, as a result of contact with excessively hot metallic surfaces.

Steel carbonising apparatus, which is constructed with the above-mentioned factors kept in view, has therefore only to endure such temperatures as boiler-plate of good quality stands quite well.

The durability of such apparatus is perfectly satisfactory, and if it is skilfully constructed the cost of maintenance is rarely higher than that of brickwork plant, which constantly needs repair.

3. Dimensions and Performance of the Carbonising Apparatus.—The dimensions of the steel or brickwork containers differ very widely, as is evident from the fact that the capacity of carbonising plants in practical operation at the present day varies from 1·5 to 400 cu. metres.

Carbonising apparatus of large capacity was employed at a comparatively early period, examples being the types of plant designed by Schwartz, Reichenbach and Hessel. These forms of apparatus proved unsuccessful however, probably for the reason that, at that time, no one possessed the experience which is essential to the operation of large apparatus in view of the violent nature of the reaction at one stage of carbonisation; and it is possible that the older operators had not sufficient patience to acquire that experience.

At any rate, it became almost universal practice to carbonise wood in small charges, and it is only comparatively recently that an increasing tendency to employ apparatus of large capacity has been shown, chiefly as a result of the progress made in that direction by Sweden and America.

It was believed that if the diameter of the apparatus exceeded a certain limit, a sufficient amount of heat could no longer be transmitted to the wood by the walls of the container, at any rate within a reasonable time.

On the other hand, the large kilns, in which the charge is heated by direct action of furnace gases, demonstrated that in carbonising wood it is unnecessary to rely solely on indirect transmission of heat by a metal shell, but that gases heated to a suitable temperature—whether furnace gases or the gas and vapours produced during the process itself—can serve as the agents for transmitting the heat.

As a result of experience it is now generally recognised that, during the process of carbonisation, the strongly heated volatile

products are able to play a large part in transmitting heat, as long as opportunity is provided for these products to part with their heat before leaving the apparatus.

This object may be achieved by taking off the distillation products from the bottom instead of from the top of the carbonising apparatus, and by arranging that the heat is supplied to the apparatus also at the bottom.

In this way, circulation is set up in the apparatus. The gases and vapours naturally rise to the top of the apparatus and are then compelled to pass down again, and the length of the path by which they must travel from their point of origin to the point of exit affords ample opportunity for the products to give up heat to the wood.

By observing these conditions it was found possible to carbonise any quantity of wood satisfactorily, quite independently of the diameter of the carbonising apparatus. As a result, apparatus of large capacity has again been adopted in recent years.

The smallest carbonising apparatus in operation is the horizontal steel retort (diameter, 1 metre; length, 3 metres) which holds about 1.5 cu. metres of wood and is charged by throwing in the wood. The largest plants are the Swedish "Carbo-ovens" (Fig. 9, p. 143), which are vertical steel cylinders holding 400 cu. metres upwards.

All other forms of carbonising apparatus, whether of steel or of brickwork, rank in size between these two.

Well-known types are the French vertical portable retorts of 5 cu. metres capacity (Fig. 12, p. 155); the large horizontal steel retorts of 25-50 cu. metres capacity, which can be discharged and charged by mechanical means immediately after the process is completed (Fig. 11, p. 150); the vertical steel retorts, heated by means of vertical radiators, which have a capacity of 50 cu. metres and are discharged only *after* cooling (Fig. 10, p. 145); also the various types of brickwork plant (Schwartz, Reichenbach, Ljungberg, Pipe-ovens, American kilns, etc.), varying in capacity from 200-400 cu. metres, which are described in detail in Chapter XII.

The choice offered in regard to carbonising apparatus is certainly not a small one, and it is not always an easy matter to choose the right type of apparatus for the particular purpose in view.

If high-grade charcoal is the main object of manufacture and

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the by-products are of little importance, a very large apparatus possibly constructed of brickwork—such as the Carbo-oven, Schwartz kiln, Reichenbach oven, or a variety of one of these plants—will always be selected, since in these cases it is necessary to allow the charcoal to cool in the container itself, with the result that the quality of the product is enhanced.

If charcoal and by-products are of equal importance, the large horizontal steel car-retorts (25–50 cu. metres capacity) or the vertical steel retorts fitted with vertical radiators (50 cu. metres capacity) will be employed.

Horizontal or vertical steel retorts of small capacity (1.5–5 cu. metres) are no longer seriously considered for large factories, and have been replaced without hesitation by the large horizontal car-retorts.

The most important types of modern steel carbonising chamber are the horizontal car-retort and the Carbo-oven.

So far, we have only considered the *capacity* of the apparatus, but not its *performance*—expressed as the amount of wood which any particular apparatus is capable of carbonising per twenty-four hours.

The cycle of operations, including charging, distillation and discharging, for:—

(a) a small horizontal retort of 1.5 cu. metres capacity occupies	12–16 hours.
(b) a small vertical retort of 4 cu. metres capacity occupies	12–16 „
(c) a large horizontal retort of 30 cu. metres capacity occupies	20 „
(d) a large vertical retort of 300 cu. metres capacity occupies	380 „
(e) an American kiln of 300 cu. metres capacity occupies	450 „

From these figures it follows that the *performance* per day of 24 hours for:—

(a) =	2.57	cu. metres of wood.
(b) =	6.85	„ „
(c) =	36	„ „
(d) =	19	„ „
(e) =	16	„ „

This table shows that the greatest performance is not obtained with the largest forms of carbonising apparatus. This is due to the fact that these types of plant cannot be discharged until the enormous mass of charcoal produced is quite cold.

Since the period of cooling extends over several days, it is naturally impossible to utilise the apparatus to the fullest extent ; moreover, serious loss of heat is also incurred owing to the necessity of heating up the apparatus again for every new operation. Except in those cases where a system of several ovens is employed, the working costs of large plant of this type are increased still further owing to the very considerable difference in the number of workers required during the periods of charging, distillation, cooling, and discharging respectively. If only one oven is used, the number of workers which must be employed for charging the oven is often greater than the number for which occupation can be found during the periods of distillation, cooling and discharging.

The more nearly continuous its operation, the more practicable is the plant.

In the case of the *small horizontal retorts*, the small amount of wood forming the charge is introduced by hand. After the process is finished, the comparatively small amount of charcoal is discharged immediately into iron boxes, in which it cools out of contact with the air. In this manner almost continuous operation is attained.

Vertical retorts of 4-5 cu. metres capacity are also charged by hand, the wood being carefully arranged in layers. The retort is portable and is lifted out of the brickwork setting after every operation and allowed to cool in the open. It is replaced immediately by a fresh retort which has been charged beforehand.

Here again, the process is practically continuous, but the heat stored up in the walls of the retort is lost after every operation.

The *car-retorts* represent the first form of carbonising apparatus which allows charging and discharging to be carried out by mechanical means. The wood is packed into steel cars which are introduced into the retort, either separately or as a train of cars coupled together, by means of some form of mechanical appliance. As soon as the process of distillation is finished, the train of cars containing the hot charcoal is

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withdrawn from the retort—again by mechanical means—and run into an iron chamber which can be hermetically sealed. This chamber is situated immediately in front of the retort and is similar in shape to the latter. The doors with which the chamber is provided are then closed, and the charcoal is allowed to cool out of contact with the air. Since the operation of transferring the train of cars from the retort into the charcoal-cooler occupies less than thirty seconds, scarcely any of the charcoal becomes ignited. At any rate, provided that the arrangements are satisfactory, the extent to which ignition occurs is so small that the loss of charcoal is negligible and the product suffers no damage.

With the remaining types of carbonising apparatus it is no longer possible to operate either continuously or nearly continuously. The large quantities of charcoal which are produced in these plants cannot be discharged, while still hot, at a sufficiently rapid rate; the apparatus must therefore be allowed to cool down after every distillation, before the charcoal can be withdrawn. For this reason, the performance of the largest forms of carbonising apparatus is relatively low.

Efforts have naturally been made to shorten the cooling period, which may extend from three to seven days according to the size of the plant. For example, water is introduced directly into the Swedish ovens as soon as the contents have cooled down to 120° C. In this way the temperature is brought down to 40° C. in a relatively short time, and discharging by hand can then be undertaken.

Attempts have also been made to shorten the period required for charging these ovens, by employing elevators—operated mechanically as far as possible—for lifting the wood. In this way the number of workers required for the operation is also reduced.

No mechanical appliances, however, have yet been introduced for discharging the charcoal from these large ovens; hence, for this purpose, only manual labour can be employed.

In the Müller ovens (see p. 139), which are of the Reichenbach type, cooling is accelerated by passing cold compressed air through the heating system after the process is finished. The air takes up the heat of the charcoal and is then used for predrying the wood.

This method of cooling requires a considerable quantity of

air, which is supplied by means of a fan. Considerable power is required to drive the fan and charges are incurred accordingly.

Gröndal (see p. 158) cools the charcoal produced in his continuous car-retort by means of the non-condensable gas, immediately before the latter is burnt as fuel. In this way the gas becomes preheated. Disadvantages attaching to this method, which is by no means new, are loss of charcoal and the danger of explosion. The small saving in heat which is brought about by preheating the gas (see below) does not compensate for these disadvantages.

All types of carbonising apparatus in which the charcoal must be retained until it is practically cold possess the advantage of producing charcoal of rather superior quality, since the product remains exposed to the influence of heat for a comparatively long time. As a result, the charcoal is rendered harder and richer in carbon.

On the other hand, these forms of apparatus present a whole series of disadvantages. Performance is relatively low owing to the extent of the cooling period, and in cases where only one oven is used it is difficult to utilise all the labour during that period. Owing to the particularly violent nature of the reaction at the beginning of the period of auto-carbonisation, an abnormally large and costly condenser system must be provided, unless several ovens are worked with one condenser system in common. If a separate condenser system is used for each oven, it remains idle during the period of cooling.

These disadvantages are entirely absent from the car-retort, which is capable of carbonising either small or large quantities of wood quite satisfactorily within a period of twenty-four hours; the performance of this retort is relatively high, owing to the provision of arrangements for charging and discharging by mechanical means; as it works almost continuously, the capital cost is relatively low, and it can be operated with relatively small expenditure for labour and fuel.

4. Arrangements for Heating the Carbonising Apparatus.

—As mentioned above, it is necessary to supply heat to the wood during two phases of the process of carbonisation, namely:—

(1). During the period in which moisture is being driven off and the temperature of the wood is being raised to 280°C. , and (2)—in the case of retorts—during the last period, in

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which the temperature is raised to about 400° C. for the purpose of increasing the carbon content of the charcoal.

During the intermediate period of auto-carbonisation very little, if any, heating is required.

Heating must be carried out in accordance with the different requirements of the separate periods; hence it is essential that the furnace employed for the purpose should be easily regulated.

The heat necessary for initiating the process of carbonisation and carrying it to completion is supplied in three different ways :—

1. Air is admitted to the interior of the carbonising apparatus in order that a portion of the wood forming the charge may undergo combustion.

2. Hot furnace gases, containing as little free oxygen as possible, are generated outside the carbonising apparatus and passed into the interior of the apparatus, thus coming into *direct contact* with the wood.

3. Hot furnace gases of any composition give up their heat indirectly to the wood through the medium of a metal partition, *without coming into contact with the wood*. The furnace gases and products of distillation follow separate paths.

The quantity of heat still present in the products after the process of carbonisation is completed has already been calculated on page 104. It was shown to amount to :—

9,000 kilo-calories in the charcoal.

147,440 kilo-calories in the gases and vapours issuing
from the retorts.

Total = 156,440 kilo-calories per cu. metre (400 kilos.) of air-dry wood, assuming that the volatile products of distillation leave the carbonising apparatus at an average temperature of 300° C.

A portion of this total is covered by the heat derived from the combustion of the non-condensable gases, which in practice (see p. 57) can furnish 56,100 kilo-calories per 400 kilos. of air-dry wood. Hence, 100,340 kilo-calories must still be provided in order to make up the total amount of heat required. If the plant is of the indirectly heated type (see 3, above), the flue gases, as a rule, escape at a temperature of 350° C. and contain 6.5 per cent of carbon dioxide. The thermal efficiency of coal in these conditions is only 40 per cent.

and therefore the *weight of coal* (at 7,000 kilo-calories per kilo.) necessary to provide the remaining 100,340 kilo-calories is:—

$$100,340 \div \frac{7000 \times 40}{100} = 35.8 \text{ kilos.}$$

In actual practice, however, 400 kilos. of air-dry wood can be carbonised with 20–30 kilos. of coal or even less, a proof of the occurrence of exothermic reactions during the period of auto-carbonisation.

Taking the *higher* calorific value of air-dry wood as 3000 kilo-calories, then 30 kilos. of coal at 7000 kilo-calories are equivalent to

$$\frac{30 \times 7000}{3000} = 70 \text{ kilos. of air-dry wood,}$$

representing the *weight of wood* required to carbonise 400 kilos. of air-dry wood, if the non-condensable gases are employed at the same time to heat the carbonising apparatus.

Assuming that the furnace is efficient, it will be safe to reckon that, when air-dry wood is used as fuel, the weight required will amount to about 16 per cent of the weight of wood to be carbonised.

The large American and Swedish ovens, in which the outlet for the volatile distillation products is at the bottom, consume even less fuel, because on the one hand the products, in circulating inside the oven, give up a large part of their heat which is utilised afresh, and on the other hand the products leave the apparatus at a much lower temperature.

Since the above figures indicate approximately the amount of fuel required, it should be possible without further data to calculate the grate-area necessary for the furnace, if it could be assumed that the fuel would be supplied at a uniform rate.

The rate is not uniform, however, and experience is the only safe guide for arriving at the grate-area of the furnace attached to a carbonising apparatus.

Having gained an idea of the amount of heat required for carrying out the process of carbonisation, we may now examine rather more closely the three different methods which, as mentioned above, are employed in practice for supplying heat.

The first and second methods consist essentially in carbonising the wood by means of furnace gases which contain more or less oxygen. In each case the furnace gases come into direct contact with the wood. Direct transmission of heat,

compared with indirect transmission through a metal partition (Method 3), is naturally more economical, especially as the kilns in which the former method is employed allow the furnace gases and volatile distillation products to escape at a relatively low temperature; at the same time, however, this method possesses great disadvantages.

The most serious is the presence of oxygen in the furnace gases. In practice it is impossible to operate the normal type of furnace with only the theoretical quantity of air. In consequence, more or less oxygen is always present in the gases, with the result that a portion of the more valuable products of distillation, especially wood-naphtha, undergoes combustion.

The oxygen-content of the furnace gases is always a fluctuating quantity, depending on the chimney draught and the regulation of the furnace dampers. Hence, as far as this particular method of supplying heat is concerned, the amount of oxygen entering the apparatus, and the loss of valuable products which occurs as a result, depend on the weather and the stoker—two very varying factors.

The draught required for supplying a sufficient quantity of air to the fuel is produced either artificially by means of fans, as in the American kilns, or naturally by providing each carbonising apparatus with one or more chimneys which are heated up at the beginning of the process.

If artificial draught is used, the regulation of the air supply no longer depends on the weather, thus the influence of varying weather conditions is eliminated.

Apart from the injurious effect of free oxygen, a further disadvantage of carbonisation by direct action of furnace gases is the mixing of the volatile products of distillation with the products of combustion of the fuel.

In consequence, the volatile products become very largely diluted with foreign gases, a condition which renders the condensation of the condensable constituents much more difficult and therefore necessitates a considerable increase in the size of the condensing plant; further, the fuel value of the non-condensable gases is reduced owing to admixture with nitrogen and oxygen.

Moreover, as shown on page 54, the non-condensable gases become saturated with the low-boiling components of the pyroligneous acid, the amount taken up depending on the pressure and the temperature of the gaseous mixture.

The greater the volume of gas which issues from the carbonising apparatus, the greater is the loss of valuable by-products.

In general, the yields of acetate of lime and wood-naphtha, obtained from kilns into which air is admitted, show a reduction of more than 50 per cent. The author was able to confirm this statement by carbonising wood of the same quality under parallel conditions, both with and without admission of air.

It is obvious that this method of heating the wood cannot be recommended, if the object of the process is to obtain the highest possible yield of by-products.

The simplest form of *direct heating* is that employed in the American kilns. These kilns are shaped like a beehive (Fig. 5, p. 132) and hold 300-400 cu. metres of wood. As many as eighty are connected with one common condensing plant, through which the products of distillation are drawn by means of exhausters.

In carbonising wood with furnace gases which are generated *outside* the carbonising chamber, each apparatus may possess one or more furnaces, or possibly several ovens together are supplied from one or more furnaces. These furnaces are designed to burn wood, sawdust, coal, lignite, tar, etc., according to local conditions. Any of the usual industrial types—from the simplest plane-grate furnace to the regenerative gas furnace—may be employed.

It is of the highest importance that the furnace gases should be distributed uniformly throughout the charge of wood.

Movement of the gases is effected by means of chimney draught or fans. The furnace gases pass from the fire-place along a radiating system of conduits which are covered over with arches containing suitable openings; the gases pass through the latter into the interior of the apparatus. Outlet pipes or chimneys, fitted with cut-off valves, are arranged round the periphery or possibly on one side of the kiln; they serve for the escape of the gases and products of distillation in a uniform manner at a number of different points.

These arrangements may vary very widely for the different types of carbonising apparatus, but the general principles described above hold good in every case. It is always a matter of conducting furnace gases—generated in some suitable manner—as uniformly as possible through the charge of wood to the top of the apparatus and then back again to the bottom,

whether by means of natural chimney draught, mechanical suction or forced draught.

In all cases where it is desired to eliminate the injurious effects resulting from the admixture of furnace gases and products of distillation, the heat is transmitted *indirectly* to the wood through the medium of metal partitions.

For this purpose, furnace gases are generated by burning solid, liquid, or gaseous fuel in the particular type of furnace best suited to local conditions. The gases give up a portion of their heat to the metal surfaces, which transmit it by radiation or possibly by conduction to the wood undergoing carbonisation.

This method of heating may be carried out in various ways. In one case, the wood may be regarded as occupying the interior of a heating tube around which the hot furnace gases circulate; in another case, as lying round the outside of a series of heating tubes through which the hot gases are passing. A third case may also occur, in which both the above modifications of this method of heating are employed at the same time.

The first modification is used for all types of carbonising apparatus which are known as *retorts* (Fig. 2, p. 50).

The second modification—namely, the transmission of heat exclusively through the medium of a system of iron pipes, which are imbedded in the wood and inside which the furnace-gases circulate—is employed chiefly in those types of apparatus which are constructed of brickwork, for example, in all ovens designed on the Reichenbach principle (Fig. 8, p. 139).

A combination of the two modifications is found in the Carbo-ovens and in the form of retort shown in Fig. 10 (p. 145).

On considering rather more closely the main features of these two different modifications of the indirect method of heating, the use of an internal system of heating tubes—as in a steam boiler—appears to offer distinct advantages. For example, practically an unlimited area of heating surface can be employed, thus making it possible to work with small differences of temperature between the heating agent and the walls of the heating tubes on the one hand, and between the walls of the heating tubes and the charge of wood on the other hand. By employing large heating surfaces, it is possible to work at temperatures which involve no danger of the tubes becoming red-hot—a condition which would lead to destruction

or warping, with further serious consequences, and above all to secondary decomposition of the products of distillation, as a result of passing over such strongly heated metal surfaces.

A further advantage attaching to the use of an internal heating system is the highly effective distribution of heat which such a system renders possible.

The disadvantages lie mainly in the unavoidably large number of joints present in a pipe system of this kind. If loose joints are present, air enters the carbonising apparatus and causes loss of the products of distillation. Moreover, in order to repair these joints the plant must be thrown completely out of action.

At a temperature of 400° C. difficulties arise in regard to the luting of the joints, and considerable expansion also takes place; in consequence each joint may become a constant source of leakage.

In spite of these disadvantages, the possibilities of this system of heating deserve the attention of the wood-distillation industry, since, in course of time, the above-mentioned objections can undoubtedly be overcome.

The method which has usually been adopted up to the present for heating the charge indirectly consists in circulating furnace gases round a horizontal or vertical steel cylinder. Here again, as emphasised on page 111, the largest possible heating surface must be provided, so as to avoid overheating and, consequently, secondary decomposition of the products of distillation. The dimensions of an internal heating system are independent of the capacity of the carbonising apparatus; if, on the other hand, the plant is designed for external heating, capacity and heating surface are essentially interdependent.

The area of heating surface and the capacity are governed by the external form and dimensions of the carbonising chamber.

With the same capacity in both cases, a carbonising chamber of smaller diameter possesses greater heating surface than a chamber of larger diameter.

Hence, for the same performance, the apparatus of smaller diameter can be operated effectively with furnace gases at a correspondingly lower temperature.

Durability of the plates and yields of products are inversely proportional to the temperature of the furnace gases—a rule which is confirmed in practice.

The correct relation between capacity and heating surface

can be attained by regulating either the diameter of the carbonising cylinder or the period of distillation.

To heat either a vertical or horizontal cylinder uniformly is a matter of considerable difficulty, which becomes greater as the size of the apparatus and the initial temperature of the gases increase.

Practical experience has shown that heating should always begin at the bottom and never at the top, since the latter will in any case always be the hotter.

It is also essential that the furnace be so designed as to exclude the possibility of fine-pointed flames coming into contact with the steel plates, otherwise the carbonising apparatus will be destroyed in a comparatively short time.

Sufficient space must therefore be left between the carbonising apparatus and the point at which the flames originate, so that the flames may die out before they can strike the walls of the cylinder; or else provision must be made for breaking the flames by employing perforated arches, etc. This problem is often somewhat difficult, even for technologists who are experts in furnace construction.

It is still more difficult to ensure uniform circulation of the furnace gases round the chamber. One method—frequently employed for vertical retorts—is to allow the undivided stream of gas to circulate spirally round the apparatus.

In these conditions the furnace gases, while at high initial temperature, strike the lower part of the carbonising apparatus. The absorption of heat inside the apparatus cannot keep pace with the supply of heat from the outside, and unless this portion of the apparatus is protected by means of firebrick against over-heating, it is impossible to prevent the plates from becoming red-hot, warping and finally burning through.

In general, spiral circulation of the furnace gases round the carbonising apparatus has not proved particularly satisfactory.

Uniform heating is more easily attained if the furnace-gases, when free from fine-pointed flames, are broken up into several jets and the latter are driven forward independently. In this way, concentration of the whole quantity of heat on one spot alone is avoided, since the heat is distributed at numerous different points according to the number of separate jets formed.

In this principle lies the secret of uniform heating, and it must be admitted that the principle is more simple to explain than to carry out.

Vertical retorts are most satisfactorily heated through the medium of a perforated arch. The fire-place is situated under the arch, and sufficient space is allowed between the arch, and the fire-place to ensure that fine-pointed flames cannot come into contact with the cylinder. The furnace gases pass through a suitable number of small holes in the arch, stream upwards, and escape through a series of adjustable ports situated in the upper portion of the periphery of the oven.

This method of heating the retort is similar in principle to the heating of a crucible over a wire gauze in the laboratory.

Horizontal retorts can be satisfactorily heated in the same manner as a combustion-tube in carrying out an organic analysis.

The furnace gases, generated in a suitably situated furnace, pass into a channel lying beneath the retort and thence through a large number of small openings, the correct size of which has been ascertained in practice. The gases pass round the walls of the retort to the top of the brickwork setting, whence they are led off by a main collecting flue.

As a general rule, the chimney draught serves to effect the movement of the furnace gases round the carbonising chamber or through the internal heating system.

In cases where gas-firing is adopted—an advantageous method for large plant—artificially induced or forced draught has also been employed latterly. Forced draught is particularly suitable for effecting uniform distribution of the furnace gases throughout the heating space of very large plant.

Artificial draught, however, whether produced by suction or by pressure, is always costly, since the high-pressure fans or exhausters used for this particular purpose are of large capacity and, consequently, consume a considerable amount of power. For each particular case under consideration it is advisable, therefore, to ascertain precisely whether the advantages offered by these complicated systems of firing are really so great that the expenditure on the generation of power is covered.

The illustrations of various types of carbonising apparatus given in succeeding chapters will serve to explain still further the nature of the furnace arrangements, both for the direct and indirect methods of heating.

5. Removal of the Distillation Products from the Apparatus.—The course of the process of wood-distillation

is influenced to a considerable degree, not only by the methods used for supplying heat to the apparatus, but also by the manner in which the products are conducted away from the apparatus. The latter particularly affects the order of appearance and the quality of the distillation products.

In the large majority of cases the outlet for the volatile products of distillation is placed at the top of the carbonising apparatus, whereas the heat is always supplied at the bottom. The gases and vapours, which are evolved as a result of applying heat, usually indirectly, ascend and leave the apparatus at once. In every carbonising apparatus the upper portions of the charge are dried first; consequently, these portions are the first to assume a higher temperature and the first to become carbonised. All gases and vapours generated in the carbonising apparatus must pass through this zone of maximum temperature, before leaving the apparatus and reaching the condensing plant.

The escaping mixture of gas and vapour has therefore no opportunity to part again with the heat which it has taken up. As a result, the temperature of the products issuing from a carbonising apparatus fitted with a top outlet is already far above 100° C. shortly after the process has begun; and it is sufficiently high to enable the stream of gas and vapour to saturate itself with tarry matter. The latter remains in a state of vapour, even after leaving the apparatus, and passes with the other volatile products into the condenser; or it may be separated by means of some special arrangement such as the patent tar separator,¹ before the pyroligneous acid is condensed.

The zone of high temperature gradually becomes greater—carbonisation proceeding from above downwards—and the gases are therefore compelled to pass through a layer of strongly heated wood or charcoal, which is constantly increasing in thickness. Continuous increase in the temperature of the escaping products, and the evolution of pyroligneous acid, wood-gas and wood-tar *simultaneously*, are the immediate results of placing the vapour outlet at the top of the apparatus. In an apparatus of this type the wood does not become dried in the first place and then carbonised, but the two processes tend to run *side by side*; and scarcely any circulation of the mixture of gas and vapour takes place inside the apparatus,

¹ German patent 189303.

since the mixture seeks to reach the outlet by the shortest path.

The use of top outlets entails a relatively large consumption of fuel, owing to the comparatively high temperature at which the distillation products leave the apparatus. Moreover, the high temperature of these products may easily cause the delivery pipes connecting the carbonising apparatus with the condensers to become blocked with tar-coke.

Coking takes place owing to a certain amount of tarry vapour separating in liquid form from the main stream of vapour and gas. The liquid tar runs through the pipes with a much lower velocity than the main bulk of the products, which still remain in the form of gas and vapour. The process which then takes place is equivalent to passing a large quantity of strongly heated gas over a relatively small quantity of tar; all volatile components are removed from the tar and the latter is converted into hard-pitch or coke, according to the prevailing temperature.

On the other hand, a top outlet enables the distillation products to leave the apparatus by the shortest path. These products only remain in contact with the more or less overheated walls of the carbonising apparatus for a comparatively short time, and the chances of secondary decomposition are reduced accordingly.

A top outlet is employed when the production of tar ready for sale, directly from the carbonising apparatus, is of no importance, and when there is no desire to obtain the highest possible degree of fractionation of the products of distillation.

In carbonising hardwood, neither of these factors comes into consideration. Hence, for this class of wood, top outlets are practically always used, provided that the apparatus is designed for *indirect* transmission of heat to the charge.

On the other hand, hardwood carbonisation apparatus which provides for *direct* heating of the charge, either by means of furnace gases or by admitting air, is fitted with bottom outlets, the object being to facilitate the carbonisation of the wood by causing the volatile products of decomposition to circulate inside the apparatus.

A bottom outlet is a necessity for all types of carbonising apparatus which operate with very large charges (100-400 cu. metres). In these cases it is advisable, on account of the large diameter, to facilitate the process of supplying heat

to the charge by causing the volatile products to circulate before leaving the apparatus.

The bottom outlet, however, is found chiefly in apparatus which is employed for the distillation of softwood.

When richly resinous softwood is carbonised, the immediate purpose of the bottom outlet is to permit any rosin, which may be melted out of the wood as the temperature gradually increases, to escape from the apparatus without decomposition, in order that it may be utilised as pitch.

Apart from rosin (abietic anhydride), however, oil of turpentine is also present as an original component of softwood.

During the process of carbonisation, oil of turpentine is evolved at a lower temperature than that required either to melt out the rosin, to effect decomposition of the latter into volatile rosin oils, or to bring about formation of tar from the components of the wood. The smaller the amounts of wood-tar and rosin oils in the oil of turpentine, the greater is the value of the product. In view of these facts, bottom outlets are preferred for softwood carbonising apparatus, since with the outlet in that position, there is less tendency for the different stages of carbonisation to overlap, and the products of distillation come over in more sharply defined fractions.

In all types of apparatus which are provided with bottom outlets and to which heat is supplied—either directly or indirectly—at the bottom, the hot gases and vapours endeavour to pass upwards, exactly as in apparatus fitted with top outlets. As the stream of gas ascends, it comes into contact with layers of wood which contain successively decreasing amounts of moisture and which exhibit a gradual increase in temperature in proportion to the decrease in the moisture-content.

After rising to the top of the oven, the gases and vapours are compelled by the action of the natural, or artificially generated, draught to descend again. In passing downwards, the gases and vapours come into contact with layers of wood which contain successively increasing amounts of moisture. The gases heat and dry the wood and become cooled themselves in the process.

Finally, the gases and vapours escape through the bottom outlet, but the temperature of the mixture (about 100° C.) is now below the dew point of the tarry vapours.

The result is that a large proportion of the tar separates

out on the bottom of the outlet pipe, before the pyroligneous acid and oil of turpentine vapours pass into the condensers.

As long as a sufficient quantity of wet wood is present in the apparatus, the temperature cannot rise to the decomposition point of either the wood or the rosin. In consequence, the main bulk of the oil of turpentine is vaporised *before* the temperature is reached at which decomposition of wood or rosin sets in, and the product consists of comparatively pure oil of turpentine—or pine oil—containing very little admixed rosin-oils and tar.

Starting from the top, the charcoal zone gradually spreads towards the bottom, and in proportion as this zone increases in thickness, the more or less moist wood lying below decreases in quantity.

As carbonisation proceeds, the gases passing down the apparatus at a relatively high temperature no longer find a layer of wet wood sufficiently thick to absorb the heat of the gases and cool the latter. Hence, towards the end of the distillation, the temperature at which the gases and vapours leave the apparatus rises to such an extent that eventually it exceeds the dew-point of the tarry vapours.

At this stage, the tar no longer separates between the carbonising apparatus and the condenser. It passes over, together with the oil of turpentine and pyroligneous acid into the condenser, and can only be separated *after* condensation, partly by taking advantage of the difference in specific gravity and partly by distillation.

The shorter the period over which this phase is allowed to extend, the better are the results.

The effects of placing the outlet at the bottom of the apparatus may be summarised as follows :—

1. Fractional carbonisation.
2. Recovery of comparatively pure oil of turpentine, which is either free from, or contains only a very small amount of, rosin oils and tar.
3. Recovery of tar mostly ready for sale and containing comparatively little pine oil, acid and water.
4. Recovery of pyroligneous acid comparatively rich in acetic acid, owing to the possibility of gradually pre-drying the wood and thus removing a large part of the water practically free from acetic acid.
5. Saving in fuel, as a result of utilising the heat contained

in the distillation products, while the latter are circulating inside the apparatus before reaching the outlet.

A bottom outlet prevents coking of the tar owing to the low temperature at which the distillation products leave the apparatus during the greater part of operation. Hence, the delivery-pipes are more easily cleaned and tar of better quality is obtained.

For large carbonising chambers (100 cu. metres capacity upwards), the bottom outlet proves a distinct advantage with either hard- or softwood.

On the other hand, carbonising plant of moderate diameter not intended for such enormous charges—especially horizontal retorts designed for the treatment of hardwood—gives at least equal results with top outlets.

6. Types of Carbonising Apparatus in Use at the Present Day.—The most important sections of a carbonising apparatus have been described in the present chapter. An attempt will now be made to classify the various types of apparatus employed in practice, and with the aid of this scheme of classification to enter into somewhat closer detail concerning the more important forms which it includes.

It is possible of course that many other forms exist with which the author is unacquainted, or concerning which he has no information. The table given below, however, includes the best known designs.

In the following chapter the various forms of carbonising apparatus are described in accordance with the divisions of the table.

CLASSIFICATION OF THE VARIOUS TYPES OF APPARATUS EMPLOYED AT THE PRESENT DAY
FOR THE CARBONISATION OF BILLET-WOOD.

I. For intermittent operation.	II. For nearly continuous operation.	III. For continuous operation.
<p>A. Brickwork containers.</p> <ul style="list-style-type: none"> (a) Heating by admission of air to the wood. (b) Heating by direct action of furnace gases on the wood. Brick kilns. (c) Heating by means of internal radiators. (Pipes, pockets.) Brick kilns. (d) Heating by means of sale wall of brick-work. 	<p>B. Steel containers.</p> <ul style="list-style-type: none"> (a) Stationary. (b) Portable. 	<p>C. Vertical Steel cylinders.</p> <ul style="list-style-type: none"> (a) Without admission of air to the charge. (b) With admission of air to the charge.
<p>American kilns.</p> <p>Kilns of the Schwartz type.</p> <p>Ottobaska kiln.</p> <p>Ljungberg kiln.</p> <p>Ovens of the Reichenbach type.</p> <p>Pipe ovens, Leschhorn oven.</p>	<p>(a) Capacity for charging and discharging by hand.</p> <p>(b) Capacity for charging and discharging mechanically.</p> <p>(c) Rotatory type.</p> <p>Wood contained in cars, charged and discharged mechanically.</p> <p>Small horizontal retorts.</p> <p>Car-retorts.</p> <p>Larson retorts.</p>	<p>Gründal retorts.</p> <p>Wood gas producers with recovery of by-products.</p>

CHAPTER XI

CARBONISING APPARATUS FOR SPLIT BILLETS, ROUND BILLETS, BRANCHES, SLABS, AND WOOD OF SIMILAR FORM

I. FOR INTERMITTENT OPERATION

ALL forms of apparatus belonging to this category are employed essentially for the manufacture of high-grade charcoal; the recovery of by-products is only of secondary importance.

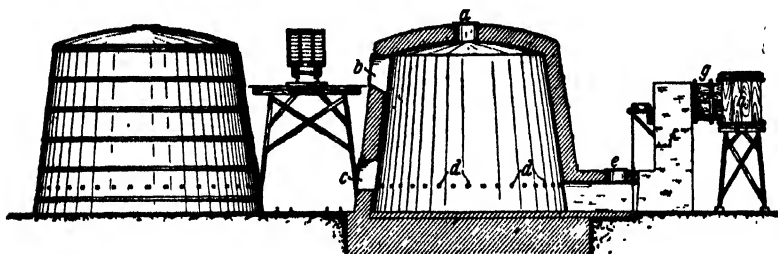


FIG. 5.—AMERICAN KILN.


These forms of apparatus only allow the charcoal to be discharged after it has cooled. Between the completion of one operation and the introduction of a fresh charge, a more or less protracted period of cooling elapses, depending on the size of the charge. In consequence, the process can only be carried on intermittently.

A.—BRICKWORK CARBONISING APPARATUS.

(a) *Brickwork kilns operated on the principle of the "Meiler," the necessary supply of heat being obtained by burning a portion of the charge.*

This form of kiln is shown diagrammatically in Fig. 5.

It consists of a brickwork chamber, shaped like a beehive, with an opening at the top through which the wood is

kindled and which can be closed by a plate *a* luted with clay. Below is an opening provided with a door *b* through which the charge of wood is introduced, and level with the bed of the kiln is another opening, with a door *c*, through which the charcoal is discharged; *b* and *c* are made of iron plate and are held tight against the brickwork by means of flat iron hoops and a luting of clay. Round the kiln is a ring of holes *d* which can be closed or opened as desired by means of bricks of corresponding shape. The brick outlet pipe for gases and vapours leaves the oven at the bottom; it is shaped thus  and is provided with a damper *f* and a trap *e*. This pipe delivers into the main vapour pipe *h*.

These kilns are used largely in the United States—especially in Michigan—for manufacturing charcoal for the iron-smelting industry. The capacity of the kilns varies from 50 to 90 cords (180–325 stacked cu. metres).

The wood is usually conveyed directly above the kiln in the railway-trucks in which it arrives, and is then dumped into the kiln through the opening *b*. Before charging the kiln, any partially carbonised billets which remain over from the previous operation and a quantity of light billet-wood 150–200 mm. in diameter are spread over the bed.

After charging is completed, the damper *f* is closed, *e* and *a* are opened, and the wood is kindled through *a*; *a* and *e* are allowed to remain open as long as practically nothing but water vapour is evolved. During this period the wood only becomes pre-dried. As soon as the escaping fumes contain acetic acid in sufficient quantity to be worth recovery—which may be recognised by the colour of the vapour evolved from *a*—*a* and *e* are closed and the damper *f* is opened, thus making connection with the collecting pipe *h* which is constructed of wood. The process is conducted by systematically opening and closing the air-ports *d*. As in all apparatus with bottom outlets, carbonisation proceeds from above downwards.

Ten of these kilns are arranged in a row, along which runs a collecting pipe for the products of distillation. Four collecting pipes from four rows of ovens unite in a central pipe which may possibly also receive the products from four other rows, each containing ten kilns. The central pipe splits up into several branches which lead to a central condensing system. The latter consists of a number of tubular condensers (see




Fig. 19, p. 186) so constructed that the vapour passes round the tubes while the water flows through them. For forty kilns, each of 300 cu. metres capacity, it is usual to provide four systems, each comprising seven condensers connected in series. At the end of each system is a fan which draws air through the openings *d* in the wall of the kiln, and the products of combustion and carbonisation through the outlet pipes, collecting pipes and condenser system. The provision of a central condenser system not only overcomes the difficulties associated with the occurrence of a period of violent reaction, but also permits the condenser plant to be utilised much more efficiently than is possible with separate condensers, which, in the case of kilns operating intermittently, stand idle while the charcoal is cooling. Another advantage of central condensation is its entire independence of the state of the weather, owing to the use of artificial means for inducing inflow of air and movement of the products of carbonisation. In this way a whole series of injurious factors is excluded.

The total period of operation—charging, carbonisation, cooling and discharging—for a kiln of about 300 cu. metres capacity is 17–20 days.

Where the objects of the wood-distillation process are to manufacture very large quantities of charcoal (the factory inspected by the author produced about 100,000 kilos per day) and to recover the by-products at the same time, it is doubtful if any other type of kiln can compete with the "American kilns" as regards capital cost, costs of labour and supervision, uniform operation, etc.

(b) *Brickwork kilns heated by furnace gases generated outside the kiln.*—This group (I A b) differs from the previous group (I A a) in that the heat required for carbonising the wood is not derived from the combustion of the wood forming the charge, but is generated from some form of fuel in a special furnace situated outside the kiln. The fuel is usually wood of inferior quality to that used for carbonisation, and possibly sawdust. Only in this respect are the forms of apparatus included in this group superior to the members of group I A a.

Carbonising plant belonging to group I A b is found chiefly in Sweden. This group is represented by numerous different forms, but in every case the design may be traced back to that of the *Schwartz* kiln, which has been known since 1820.

Several of these kilns, constructed on the principle of

the *Schwartz* kiln, are described in a publication by Hilding Bergström.¹

The *Schwartz kiln*² consists of a brickwork chamber, possessing the form of a muffle furnace with a half-egg-shaped cross-section. The length of the kiln is twice the width, and the bed is raised in the centre and inclines to each of the shorter sides. At the middle of each of the longer sides is a fire-place. The products of combustion and distillation escape through pipes, which lead off from the centre of the shorter sides of the rectangular bed. The tar separates and is run off through a siphon, immediately after the gases and vapours leave the kiln; the other products still remaining in a state of vapour pass into the condenser, where the pyroligneous acid is condensed. The non-condensable gases pass into a chimney which is brought into action at the beginning of the process by means of a separate fire. By the action of the chimney-draught the necessary supply of air is drawn into the furnace, and the products of combustion and distillation are drawn through the condenser.

With two fire-places and only one chimney it proved a difficult matter to distribute the furnace gases uniformly throughout the charge. The provision of several chimneys and a central furnace, with arrangements for an efficient distribution of the furnace gases from beneath the bed of the kiln, led to the construction of the *Ottelinska kiln*, which is shown in Fig. 7. This design permitted much more efficient control of the furnace gases and therefore of the process of carbonisation itself.

The shape of this kiln is approximately similar to that of the *Schwartz* kiln.

The *Ottelinska kiln* is provided with only one fire-place, which is situated in the middle of one of the longer sides and is built into the kiln. The furnace gases pass, in the first place, to the centre of the rectangular bed and thence diagonally into four branch flues. The gases escape into the kiln through perforated arches, which are built over five outlets situated respectively at the centre of the bed and at the ends of the diagonal flues.

¹ "Om Kolning af Barrwed," Hilding Bergström, Stockholm, 1904.

² For a detailed description of the *Schwartz* kiln see "Chemical Technology," Vol. I, "Fuel and its Applications," by Mills & Rowan. (London, J. & A. Churchill, 1889).

At either end of the kiln is a brickwork chimney in which a draught is induced at the beginning of the operation by means of a wood fire and bellows. In addition, each of the longer sides is provided with two outlet pipes which can be opened or closed by means of throttle valves; these pipes may be constructed of iron, copper or wood. The process of carbonisation is readily controlled owing to the efficient distribution of heat and the arrangement of the outlet pipes, which can be opened or closed at will, at intervals on the periphery of the kiln.

Another member of this group, which differs in certain

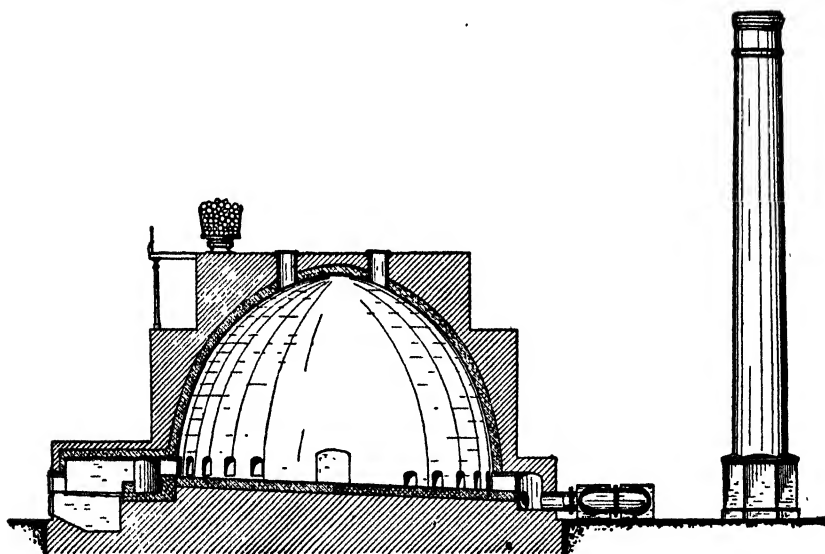


FIG. 6.—A MODIFIED FORM OF THE SCHWARTZ KILN.

respects, is the *Ljungberg kiln*. This kiln, which followed the lines of the Schwartz kiln, was originally constructed as a ring kiln and was intended to be operated continuously on the same principle as the Hoffmann kiln.

In practice, however, this principle has been abandoned, and the *Ljungberg kiln* is only worked as a system of ovens in so far as several carbonising chambers of 170 cu. metres capacity—but each with its own separate furnace—are operated together in one set.

As in the American kilns, the combustion and distillation products pass into a central collecting pipe which is connected with an exhauster.

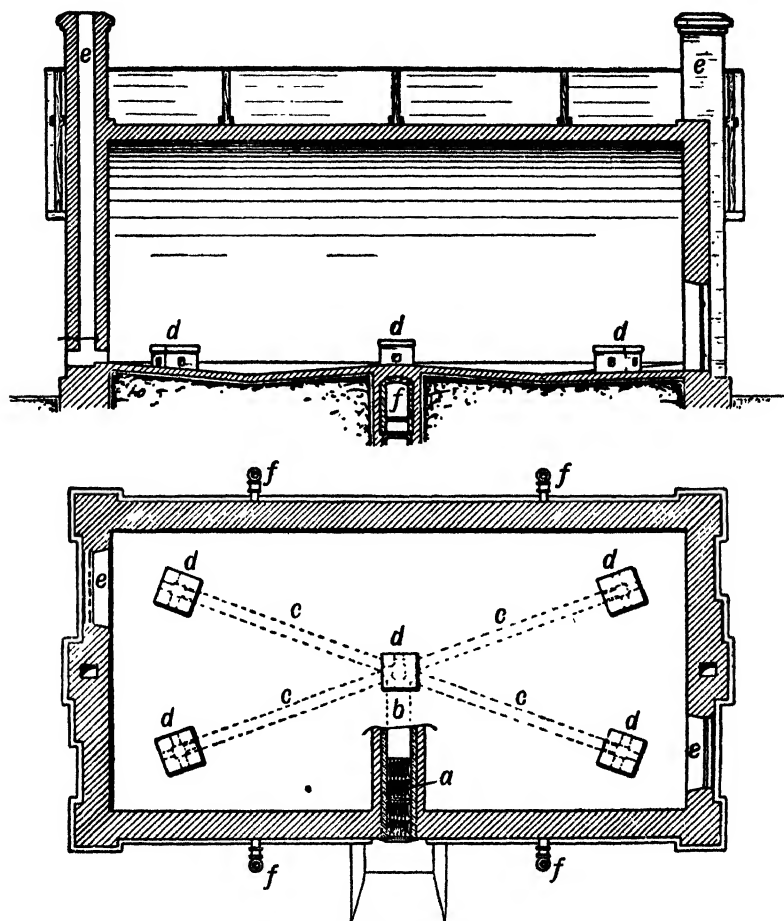


FIG. 7.—OTTEKINSKA KILN.

a, furnace ; *b*, main flue ; *c*, diagonal flues ; *d*, outlets for furnace-gases ; *e*, brickwork chimneys ; *f*, outlet pipes.

The bed of the Ljungberg kiln is inclined like a very steep roof, which renders it possible to discharge the charcoal easily and rapidly through apertures situated along the lower edge of the bed and provided with iron doors.

(c) *Brickwork carbonising apparatus heated by means of radiators*.—All types of carbonising apparatus belonging to this group may be traced back to the Reichenbach oven, which was one of the earliest forms of carbonising apparatus (see p. 7).

The advantages attaching to the use of brickwork carbonising apparatus heated by means of radiators have already been explained on page 122. The essential feature of this type of plant is the provision of a radiator system inside the brickwork carbonising chamber; in this way the furnace gases are prevented from coming into direct contact with the wood, and the products of combustion and of distillation follow separate paths.

The *Reichenbach oven*¹—the oldest (1820) representative of this type of apparatus—consisted of a brickwork chamber which contained a heating system composed of a series of coils extending through the interior of the chamber. The coils were made up of horizontal cast-iron pipes, screwed together and connected at the ends by cast-iron bends. The furnace gases entered from below into this heating-system, which was about 600 mm. in diameter and delivered into a flue which carried off the products of combustion.

The Reichenbach oven had a capacity of about 50 cu. metres and was provided with two separate radiator systems, each with its own furnace. The oven was covered over at the top with cast-iron plates. The bed sloped down to the centre, where a copper pipe, which formed the outlet for the products of distillation, was situated. In order to ensure efficient distribution of the heat, the furnaces connected with the radiator systems were placed one on either side of the carbonising chamber.

Exactly similar in principle are the so-called *Pipe-ovens* (Fig. 8) recently introduced into Sweden and Finland. The only point of difference is that the radiator system is confined to the lower portion of the oven, whereas in the Reichenbach oven the radiators extended to the upper portion.

The Swedish *Pipe-ovens* are also provided with several outlets for the volatile products of distillation, arranged in exactly the same manner as in the Ottelinska kiln.

The *Leschhorn oven*² also belongs to this group. Ovens of

¹ See also Muspratt's "Chemistry," Vol. I, p. 19 (William Mackenzie, Glasgow, etc.).

² German Patents, Nos. 67,099 and 79,184.

this type are in operation at Pluder, near Oppeln. The distinguishing feature is the heating system which consists of a number of horizontal pipes passing through the chamber. The hot gases, which are generated in special furnaces, pass into a single flue and thence into the heating pipes. At the other end of the system, the gases unite again in a single outlet flue, finally passing into the chimney. By means of dampers the heating pipes can be put in or out of circuit in groups, thus making it possible for the heat to be directed towards the top or the bottom of the oven.

Another characteristic feature connected with the operation

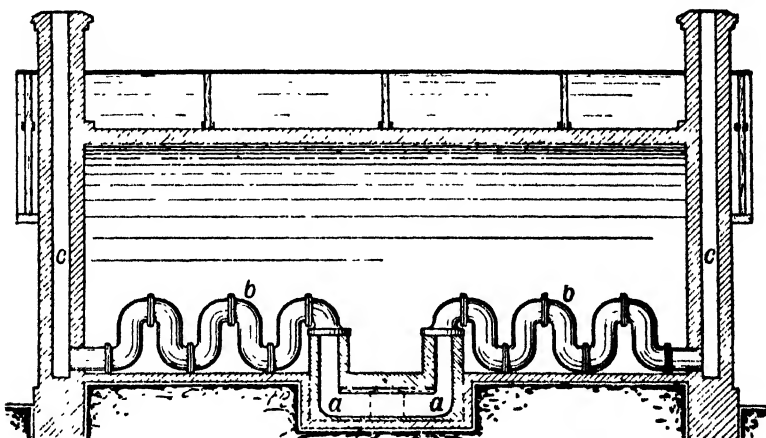


FIG. 8.—SWEDISH "PIPE-OVEN."

a, a, flues ; *b, b*, radiators ; *c, c*, chimneys.

of this oven is the practice of passing non-condensable gases, from the condensers attached to other ovens, through the heating system, for the purpose of cooling the charcoal more rapidly after the process is finished.

The gases absorb heat from the charcoal and cool the latter.

This method of cooling the charcoal is not a new idea ; it has been suggested previously in Dingler's "Polytechnisches Journal."

An apparatus of unique construction, belonging to group I A c, has been patented by G. Müller¹ and installed on an experimental basis in a Swedish sawmill. This apparatus also

¹ German patent 173,237.

makes use of radiators for supplying heat to the charge. These radiators are arranged to form shafts, which are really vertical rectangular retorts, inside a cubical brickwork chamber. The radiators consist of flat heating boxes which are combined into a series of separate systems. One oven contains sixteen shafts, the walls of which are formed by the flat radiators.

Hot gases, derived from some convenient source, pass through a main pipe into four branch pipes, each of which is connected with the radiators belonging to four shafts. The gases, after parting with their heat, pass from the radiators through a similar arrangement of pipes.

In order to ensure the greatest possible uniformity of heating, and to overcome more easily the frictional resistance offered by the many separate radiators, the furnace attached to the apparatus is operated by forced draught.

The wood forming the charge is packed into baskets made of iron netting, which are suspended in the shafts. The shafts are closed at the top with steel plates; a luting of sand is used at the junctions of the plates and between the plates and the brickwork of the oven. Since this apparatus is specially intended for the carbonisation of softwood, the outlet for the products of distillation is situated in the bed of the oven, which slopes towards the centre.

Near the oven is a so-called pre-drier, consisting of a brickwork chamber into which the iron baskets containing the wood are introduced prior to carbonisation. The pre-drier is heated by means of the flue gases escaping from the carbonising apparatus, the chamber being fitted with an arrangement for the efficient distribution of the gases.

The first part of this drying process is carried out with the waste flue gases. As soon as the process of distillation in the carbonising apparatus itself is completed, cold air is driven through the radiators by means of the high-pressure fan which has previously been serving the furnaces. The heat of the charcoal is absorbed by the air, and as a result the cooling period for the charcoal is substantially shortened. The heat absorbed by the air is utilised again by passing the hot air through the pre-drier, whereby particularly intensive drying of the wood is effected—a matter of considerable importance in view of the very high moisture content of some of the wood used in Sweden. At the same time it is questionable if any real saving is effected by this method of utilising the heat

stored up in the charcoal, since the oven itself becomes cooled down after every operation, and the loss of heat must be made good again each time the oven is started up for a fresh operation.

As soon as the charcoal is sufficiently cool, the steel plates covering the top of the oven are lifted off with the aid of a mechanical appliance, and the baskets, now full of charcoal, are lifted out—also by mechanical means—and emptied.

The Müller oven undoubtedly possesses certain advantages, but the capital cost is high, and the fan necessary for creating the forced draught consumes a considerable amount of power.

(d) *Brickwork apparatus provided with double walls which form an external heating jacket.*—Ovens of this type—known as *tar-ovens*—are employed in East Prussia, Silesia, Thuringia and also in Russia. They serve especially for the carbonisation of richly resinous pinewood roots from which the sapwood has been removed.

The main object in operating this type of apparatus is to produce softwood tar of good quality, and pine-oil as free as possible from tarry products. Pyroligneous acid is rarely worked up from this form of plant.

These ovens have a capacity of about 30-40 cu. metres and are shaped like a beehive. The chamber is surrounded, for about two-thirds of its height, by a second wall of brick. Furnace gases, which are generated in a conveniently situated fire-place, circulate inside the space between the two walls.

As a rule the inner chamber is not quite gas-tight owing to the presence of fissures and cracks in the brickwork; in consequence, certain quantities of the more highly volatile products pass into the heating space, burn there, and thus assist the heating of the whole apparatus, though scarcely in an economical manner. Since brickwork is a very poor conductor of heat, it is obvious that the fuel consumption of these ovens must be relatively great.

The cycle of operations—including charging, distillation, cooling and discharging—for an apparatus of this type occupies about six days. The distillation products escape through a copper pipe placed at the bottom of the oven. On the under side of the pipe, at a short distance from the point at which it leaves the oven, a siphon-pipe is fitted, through which the tar runs off; on the top is a second pipe which conducts the uncondensed products—pine oil and pyroligneous acid—to

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the condensers. The tar, containing a certain amount of pyroligneous acid, flows through a series of wooden boxes in which it separates from the acid; the product is usually exported without further treatment.

B.—STEEL CARBONISING APPARATUS.

We have now to consider those forms of apparatus designed for intermittent operation, in which the carbonising chambers are constructed of steel. Here again, it is only possible to discharge the charcoal after the apparatus has cooled down.

According to the table on page 131, this class of apparatus may be divided into two groups, viz. :—

- (a) Stationary,
- (b) Portable.

The former group may be divided into two sub-groups, (a) plant of large capacity fitted with bottom vapour-outlets; (b) plant of smaller capacity fitted with top vapour-outlets.

The tar-ovens belonging to group I A d may be looked upon as the forerunners of the plant included in group I B a a. If the inner wall of the former were replaced by a steel shell, the apparatus would be very similar in construction to the Swedish *Carbo-ovens* (Fig. 9) called after the name of the company which patented the apparatus and introduced it into the industry.

This oven consists of a large steel carbonising chamber, which possesses the form of a vertical cylinder and holds 300–400 cu. metres of wood. The steel bed is saucer-shaped and at its centre is the outlet pipe for the distillation products. The cylinder is closed at the top by a steel cover which is provided with four openings for introducing the charge. The charcoal is discharged through an opening near the bottom.

Spiral flues, which can be directly regulated by means of separate dampers, run round the cylinder. The furnace is situated opposite to the charcoal discharge opening and is usually designed to burn wood; it is divided by means of a tongue into two fire-places, each with its own grate and fire-door. From these fire-places the furnace gases enter the flues and circulate round the oven.

The carbonising cylinder is covered with firebrick for one-third of its height, with the object of protecting the lower

portions against the action of fine-pointed flames and generally diminishing the effect of the furnace gases, which at this stage are particularly hot. Above the covering of firebrick the gases come into direct contact with the naked steel plate, but by this time the temperature of the gases has fallen so low that

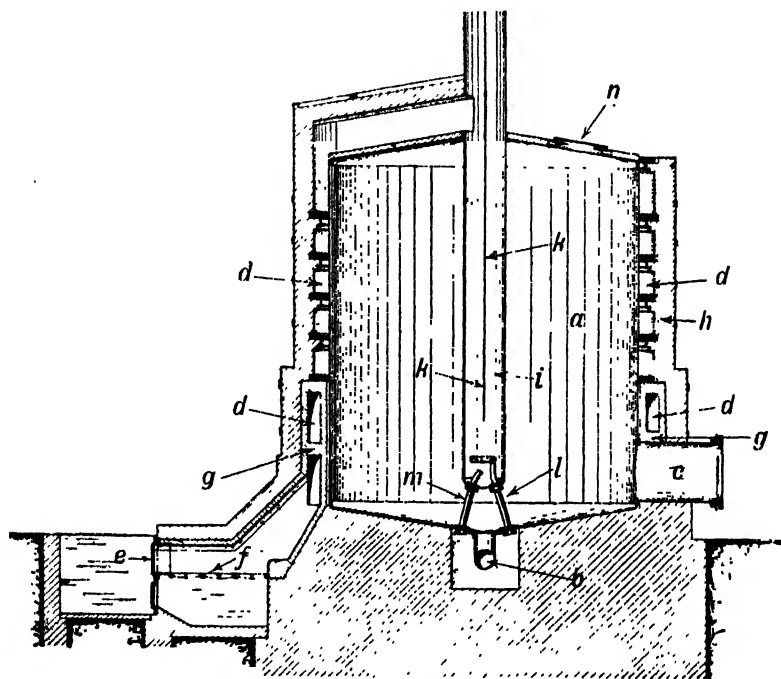


FIG. 9.—SWEDISH CARBO-OVEN. (CAPACITY: 300-400 CU. METRES.)

a, steel container; *b*, outlet pipe for distillation products; *c*, charcoal discharge opening; *d*, spiral flues; *e*, fire-door; *f*, grate; *g*, firebrick covering; *h*, outer brickwork wall; *i*, heating pipe; *k*, partition; *l*, inlet pipe for non-condensable gases; *m*, inlet pipe for air; *n*, opening for introducing the wood.

overheating and consequent damage to the plates is no longer likely to occur.

A characteristic feature of the Carbo-oven is the large vertical heating pipe situated at the middle of the oven. This pipe is divided by a central partition; it is closed at the bottom end, but is fitted with two inlet pipes through one of which non-condensable wood-gas is passed, and through the other the air necessary to support the combustion of this gas.

The pipe can therefore be heated internally by the combustion of the non-condensable gas.

The furnace gases issuing from the last flue pass into the upper portion of the central heating pipe and are forced to pass downwards owing to the presence of the partition in the pipe. The gases pass round the lower end of the partition and up the pipe again, finally escaping into a chimney together with the products of combustion of the wood-gas. Thus the Carbo-ovens are heated on the one hand by furnace gases passing round the outside of the cylinder, and on the other hand by a central radiator which derives its heat partly from the furnace gases and partly from the products of combustion of the non-condensable wood-gas.

The most striking feature of the Carbo-oven is its capacity—300–400 cu. metres—which, for an apparatus constructed of steel, is enormous.

About a dozen Carbo-ovens are in operation in Sweden for the carbonisation of softwood.

The capital cost of the oven, though relatively high, is small in proportion to the potential output.

Exactly similar in principle to the Carbo-ovens are the so-called *Bosnian Meiler-ovens*¹ (I B a β). (Fig. 10.)

The cylindrical steel chamber of the Bosnian oven holds about 50 cu. metres of wood and, like the Carbo-oven, is heated externally by the application of hot furnace gases, and also internally by means of vertical heating pipes. The outlet for the volatile distillation products is situated at the top of the oven.

The bed rises to the centre in the form of a wedge, which facilitates the removal of the charcoal through lateral discharge openings.

These ovens are worked in Bosnia. The cycle of operations—charging, distillation, cooling, discharging—for a plant of 50 cu. metres capacity occupies five to six days.

The *Drommart oven* (I B b) is also furnished with a steel carbonising chamber. In view of the manner in which it is heated, this oven belongs rather to group I A b or I A c.

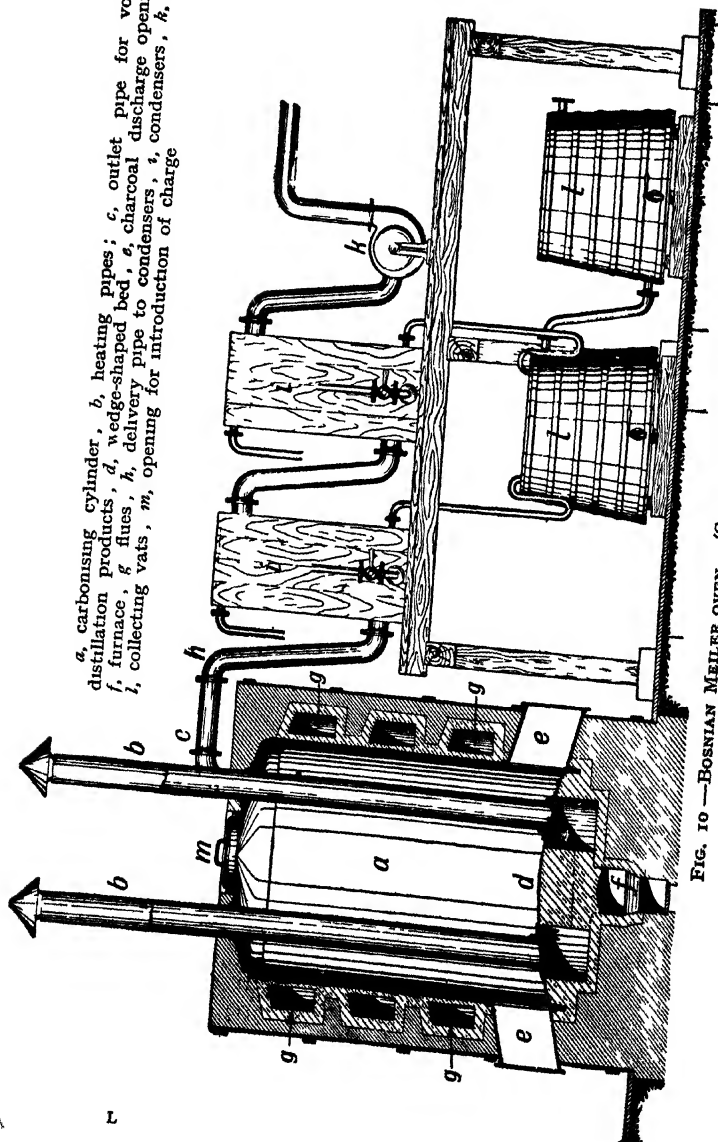
The Drommart oven—which is still used in France—consists of a beehive-shaped steel carbonising chamber holding about 50 cu. metres of wood.

The plates of which the chamber is constructed are bolted,

¹ German patent 10,649.

APPARATUS FOR BILLET-WOOD, ETC.

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a, carbonising cylinder, *b*, heating pipes; *c*, outlet pipe for volatile distillation products, *d*, wedge-shaped bed, *e*, charcoal discharge opening, *f*, furnace, *g*, flues, *h*, delivery pipe to condensers, *i*, condensers, *k*, fan; *l*, collecting vats, *m*, opening for introduction of charge

FIG. 10 — BOSNIAN MEILER OVEN. (CAPACITY: 50 CU. METRES)

not riveted, together; hence the oven can be taken apart at any time and re-erected—in other words it is portable. All other parts of the plant are likewise designed for rapid assembling and dismantling, as well as for easy transport.

The oven is heated by a kind of radiator. Hot furnace gases enter from below at the centre point of the bed, and travel to the periphery of the oven through a number of radial flues which are covered over with cast-iron plates. At the periphery each of the radial flues opens into another flue, which runs concentrically with the shell of the oven and is likewise covered over with cast-iron plates. At a short distance from its point of intersection with the next radial flue, the peripheral flue delivers into a cast-iron heating pipe. Heat is therefore supplied to the charge through the medium of the radial and peripheral flues running in the floor, as well as from the heating pipes which are embedded in the wood. The heating pipes end in bends which pass through the walls of the oven and conduct the furnace gases to the exterior. Owing to the tendency of the cast-iron plates covering the flues to work loose, this system of heating allows a certain quantity of furnace gas to leak into the chamber, with the results mentioned on page 123.

II. CARBONISING APPARATUS FOR NEARLY CONTINUOUS OPERATION

The second large group of carbonising apparatus comprises those types which, in contrast to the members of the previous group, permit of nearly continuous operation.

Continuous carbonisation of wood necessitates continuous discharge of charcoal out of contact with the air. Exposure to the action of air for any length of time would result in the combustion of at least a portion of the charcoal with consequent reduction in the yield. An alternative to the continuous process, on the one hand, and the intermittent process, on the other hand, is the *nearly continuous process* in which the charcoal is discharged immediately after carbonisation is finished.

Two methods are available for carrying out the nearly continuous process:—

(a) After distillation is finished the charcoal is discharged as rapidly as possible into iron containers which can be

hermetically sealed, thus allowing the product to cool out of contact with the air (groups II A a, II A b and II B a).

(b) The charcoal remains in the carbonising chamber, which is lifted out of the furnace-setting for the purpose of cooling and is replaced by a similar vessel containing a fresh charge (group II B b).

In method (b) the weight of the container must necessarily be kept within reasonable limits, and its capacity is governed accordingly.

It is obvious that all members of group II which are charged and discharged by *hand* must only be of small capacity, otherwise it will be impossible to avoid loss of charcoal by combustion.

The forms of apparatus included in group II may be divided, in the first place, into two sub-groups:—

II A=Horizontal carbonising apparatus,

II B=Vertical carbonising apparatus.

A.—HORIZONTAL CARBONISING APPARATUS.

The simplest examples of group II A are the small horizontal retorts which are operated in England, Germany, Austria-Hungary, Russia and, to a certain extent, in the United States. These retorts are one metre in diameter and three metres long, but the capacity is only about 1.5 cu. metres owing to the method of charging by simply throwing the wood into the retort, which results in loose packing. The period of operation is twelve hours. The steel or cast-iron door of the retort is usually held in position over the retort-mouth by means of a tongue and groove, and is fastened with swivel-bolts or hoops, clay being used as the luting material. The opposite end of the retort is closed by a cover-plate to which the outlet pipe for the volatile distillation products is riveted. The retort is also provided with a semicircular draw-plate of sheet-iron, which is riveted to the short limb of a round iron rod bent at a right angle, the long limb of which is the same length as the retort.

Very often, one pair of retorts is heated by a single furnace which is then built between the retorts. The furnace gases are conducted round the retorts, in some cases from above downwards and in other cases in the opposite direction.

As a general rule the heating is not particularly uniform, especially when the gases circulate from above downwards. Consequently it is now the custom, in the rare instances in which these small retorts are still erected, to provide a separate furnace for each retort and to pass the furnace gases backwards and forwards in a horizontal direction, as in a Cornish boiler, or else upwards through a perforated arch built beneath the retort.

Each retort is provided with a separate condenser constructed of copper piping (see Fig. 18, p. 185), but very often two of these condensers are placed in a single water-tank.

In working an apparatus of this type the sheet-iron draw-plate is first of all pushed to the back of the retort. The retort, which is still hot after the previous distillation, is then charged by throwing in billets of wood usually one metre in length. The old clay luting is removed from the groove in the retort door, a new luting is applied, and the door is closed. Distillation begins after a short time and—with a charge of 1.5 cu. metres—is usually finished in twelve hours, without having shown any signs of the violent phase of carbonisation which is characteristic of large apparatus.

Any kind of fuel may be used for heating the retort as long as the furnaces are designed accordingly.

The non-condensable gases issuing from the condensers (see p. 53) are usually burnt under the retorts.

As soon as the distillation is finished—that is, when the retort neck is cold—a rectangular or trough-shaped steel container, resting on a car-frame or fitted with its own wheels, is run under the mouth of the retort. The retort door is opened, and the glowing charcoal is discharged into the container by pulling the draw-plate forward. If the charcoal ignites it is quenched with water. The container is at once closed with a cover, the joints are rendered airtight by luting with clay or sand, and the container is then run to a convenient place for cooling. As soon as the space in front of the retort is clear, the fresh charge, standing ready on a truck, is introduced and the process begins again. After cooling, the charcoal is removed from the containers and is separated, by means of iron rakes or screens, into large and small pieces known respectively as "stick" and "breeze." It is then taken into store or filled into sacks for the market. It may also be loaded loose into railway trucks or other vehicles for transport in bulk, provided

that it has been allowed to stand exposed to the air for a sufficient length of time beforehand.¹

Owing to the small capacity of these retorts a large number is necessary for a moderate output. This entails high capital cost and also a comparatively heavy consumption of fuel as a result of working with a large number of small furnaces. Heavy costs for labour and supervision are also incurred, owing to the necessity of handling small quantities of wood and charging the retorts twice in the twenty-four hours. The short distillation period also renders it necessary to use wood of small diameter, with the result that considerable costs are incurred for splitting the wood.

In view of the many advantages offered by the horizontal retort it was obviously desirable to increase its capacity. Before this could be effected, however, it was necessary to devise some suitable method of charging and discharging at a more rapid rate than was possible in the case of the small retorts.

This problem was first solved in England, by using cars to hold the charge of wood. The cars were run into the retorts on rails laid down on the retort floor. As soon as the process was completed, the cars, then containing charcoal, were withdrawn into cooling chambers which could be hermetically sealed.

This system of operation established the principle of the car-retorts (II A b).

English factories worked with comparatively small charges; but in the United States the capacity of the retorts was gradually increased up to 50-60 cu. metres.

The author, after having had the opportunity of studying the American rectangular steel car-retorts and of becoming acquainted with their advantages and disadvantages, has introduced several improvements into this type of apparatus, which give it a more convenient form, increase its durability and render the heating more uniform. In all cases where the volatile distillation products are of primary importance, it may be claimed that the car-retort manufactured by the author's firm is at present the most efficient and cheapest form of carbonising apparatus available.

¹ The railway regulations governing the carriage of charcoal differ according to the country. In most cases a definite period is specified, during which the charcoal must stand exposed to the air before being loaded on to the trucks. The period varies according to the nature of the consignment—that is, whether it consists of "stick," "breeze," or ground charcoal.

The car-retort plant (Fig. 11) is made up of the following main parts :—

- (a) The horizontal steel carbonising chamber, fitted with a fixed cover at one end and a door at the other, or else with two doors. The chamber is provided with either one or two vapour-outlet pipes, which are situated at the side, at the top, or possibly at the end. A rail-track for the retort cars runs along the floor of the chamber.
- (b) The furnace for heating the retort.
- (c) The condenser connected with the retort.
- (d) The charcoal cooler—a steel chamber placed in front of the retort, of the same shape as the latter and fitted with a similar rail-track. The cooler is usually provided with a door at each end.
- (e) The movable section of rail connecting the retort with the charcoal cooler.
- (f) The mechanical appliances for moving the cars.
- (g) The retort-cars.

During the day, the wood is packed into the cars, each of which usually holds 7.5 cu. metres. Four cars form a retort charge. Immediately after the cars forming the previous

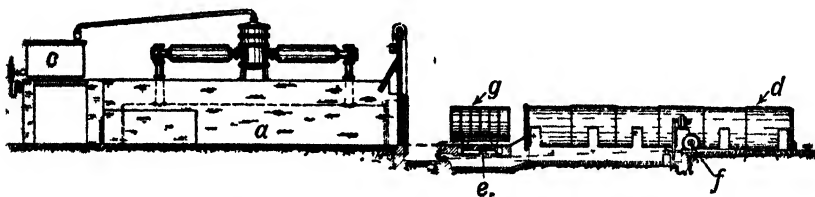


FIG. 11.—MEYER RETORT. A CAR-RETORT OF 25-50 CU METRES CAPACITY DESIGNED FOR NEARLY CONTINUOUS OPERATION AND FITTED WITH A TAR-SEPARATOR ¹

charge have been withdrawn, the four freshly loaded cars are drawn into the retort—either singly or coupled together—by means of a wire-cable operated by a winch, which may be driven electrically or by any other suitable form of power. The door, which is provided with a tongue fitting tightly into a groove in the door-frame, is then closed, and the retort is strongly heated—possibly by burning the non-condensable gas

¹ German patent 189,303.

from other retorts which are at a more advanced stage of the process, or in any other manner which will ensure uniform heating of a cylinder, 15 metres in length.

The course of the distillation process depends on the amount of moisture in the wood, the type of furnace and the method of firing.

As soon as the process in the retort is finished, the first operation is to open the charcoal cooler and remove the cars to a shed, where the charcoal is discharged and dealt with further as desired. The empty cars are run at once to the wood-yard, refilled with wood and then placed in the pre-drying chambers, which, if provided at all, are erected opposite to, or alongside, the retorts. As soon as the charcoal cooler is empty, the door of the retort is opened and the train of cars filled with charcoal is drawn into the cooler which is then closed as quickly as possible. If the arrangements for moving the cars are satisfactory, this operation occupies only a few seconds, hence it is scarcely possible for the charcoal to become ignited, and the loss due to combustion is no greater than for the small retorts of only 1.5 cu. metres capacity. Everything depends on the smooth action of the retort and cooler doors, the cars, and the hauling arrangements. Slight errors in the construction of these parts, due to lack of experience, are likely to lead to serious results.

As soon as the train of cars has been run into the cooler and the doors of the latter have been closed, four fresh cars, loaded with wood and standing ready on a branch line or in the pre-drying chamber, are pushed into the retort and firing is started.

The whole series of operations—discharging the charcoal cooler, discharging the retort, charging the retort and fastening up the doors—occupies no more than thirty minutes, if carried out by experienced workmen. Four men are required for the purpose.

For a bench of four retorts, treating 100–120 cu. metres of wood in 24 hours, these operations occupy two hours and employ four workmen. During the remainder of the period only one man per shift is necessary for firing the retorts and watching the process.

By employing this type of retort it is possible to effect a very considerable saving in the cost of labour, as the above figures demonstrate. Moreover, owing to the fact that the process is

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nearly continuous—only thirty minutes' interruption in every twenty-four hours—the capital cost of the installation and the consumption of fuel are relatively small.

The method of heating these retorts has already been described on page 124.

The car-retort plant is better adapted than any other type to utilise the flue gases leaving the retort furnaces for "pre-drying" the wood—a process which has been widely advocated during recent years. This form of apparatus also renders it quite feasible to utilise the heat contained in the charcoal for preheating the non-condensable gas, before the latter is burnt in the retort furnaces.

As pointed out on page 106 it is impossible, while maintaining a normal consumption of fuel, to *dry* the wood by means of the waste gases from the retort furnaces. The most that can be effected is a certain degree of *preheating*, which is carried out by placing the cars loaded with wood in a chamber, situated between the retorts and the chimney, around which the flue gases are allowed to circulate before entering the chimney.

The heat contained in the charcoal may be utilised for preheating the non-condensable gases by conducting the latter through a special pipe which runs along the inside wall of the cooler. The prospects of effecting economy in this way have already been discussed on page 104.

Results obtained in actual practice with the same quality of wood show that the yields of distillation products from car-retorts are higher than those obtained from small retorts; the charcoal is superior in quality, and wood of considerably greater diameter can be carbonised. Moreover, for equal output, the capital cost of the car-retort plant is smaller, and the cost of labour and the consumption of fuel are also less. Finally, with this type of plant it is possible to utilise practically every method of economising heat. For these reasons the author considers it justifiable to regard the car-retort as the best form of carbonising apparatus introduced up to the present.

Before dealing with the vertical types of carbonising apparatus mention may be made of the *rotary retorts* (II A c) which were employed by the "Trebertrocknungsgesellschaft."

This apparatus consists of a horizontal steel carbonising cylinder of 30-40 cu. metres capacity, which rotates in a furnace and, in addition, is heated internally by means of

horizontal radiators. The distillation products are taken off by means of contact valves which open systematically during the rotation of the retort. This retort had only been in operation for a short time, when the above company collapsed; it was already evident, however, that the rotary retort was quite unsuitable if high-grade charcoal was desired, as is always the case when billet-wood is carbonised. On the other hand, the yields of volatile products were very good. As far as the author is aware, the only retorts of this type in operation at the present day are in a Belgian factory, where they are employed for carbonising tannin-extract residues.

B.—VERTICAL CARBONISING APPARATUS.

The steel retorts comprised by group II B are disposed vertically and therefore bear a resemblance to the Müller oven. Like the horizontal apparatus, the members of this group exist in two distinct forms. The members of sub-group II B a are stationary, and are charged and discharged by manual labour; those belonging to sub-group II B b are portable, and are lifted out of, and introduced into, the oven by mechanical means. Although the portable retorts are charged and discharged outside the oven and mechanical transport is employed, it is impossible to use apparatus of great dimensions—as in the case of the large horizontal retorts—since the comparatively heavy weight of the charged vertical retort imposes a definite limit to its size.

The simplest type of vertical apparatus is the *stationary vertical retort* (II B a). This retort is closed at the top with a movable cover and is provided with an opening at the bottom for the discharge of the charcoal. The lower portion of the retort ends in a cone, which passes vertically through the brickwork and is fitted at the end with a horizontal lid closed by means of a screw and crossbar, similar to the arrangements on a vertical extraction plant.

In other forms the lower portion is bent into an elbow which tapers slightly and passes laterally through the brickwork; it is fitted at the end with a vertical lid. Retorts of this type are known as *beak retorts*; they were introduced by the "Trebertrocknungsgesellschaft" and are still operated in Russia.

The stationary vertical retorts (II B a) are usually set in a

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brickwork oven. A perforated arch forms the bed of the oven and the furnace is situated beneath the arch. The furnace gases pass through slits in the arch and finally escape from the oven through flues, which open at a number of points situated as high as possible on the periphery of the oven and communicate with the chimney. The outlet for the volatile products of distillation is usually placed at the top of the retort.

The retort may be charged simply by throwing in the wood, but in this way the internal space is very inefficiently utilised. A better method is to tie up the wood beforehand into bundles, of the same diameter as the retort, and to lower the bundles into the retort. After the process is finished, an iron container of suitable capacity is run under the retort; the lid is then opened, and the charcoal, which is loosened if necessary by means of suitably shaped hooks, runs into the container. The latter is then hermetically sealed, exactly as described in the case of the small horizontal retorts, and set aside to cool.

Compared with the small horizontal retorts, the advantage of this form of apparatus is that, owing to the more practical methods of charging and discharging, the dimensions of the retort may be somewhat increased—for example, up to a capacity of 4 cu. metres.

A more common form of vertical retort is the *portable type* (II B b), (Fig. 12), which is found especially in France, Belgium and Italy, but is also employed in Germany and Austria-Hungary. The main features of this type of apparatus have already been described above. The cylinder is charged outside the oven, closed with a cover, and introduced into the oven by means of some form of mechanical appliance. The short outlet pipe at the centre of the cover forms a socket, into which one end of the portable copper pipe leading to the condenser is fitted, the joint being luted with clay. More rarely, a hydraulic seal is employed. As soon as the process of distillation is finished, the delivery pipe is disconnected, the outlet in the cover closed with a lid, and the retort is then lifted out of the oven and lowered into a horizontal position in front of the charcoal shed, where it is left to cool.

When the cooling process is finished—that is, after the retort has been allowed to stand for 12-16 hours—the cover is removed, the charcoal discharged, and the empty retort then conveyed to the charging-place. As a rule, the retort, after

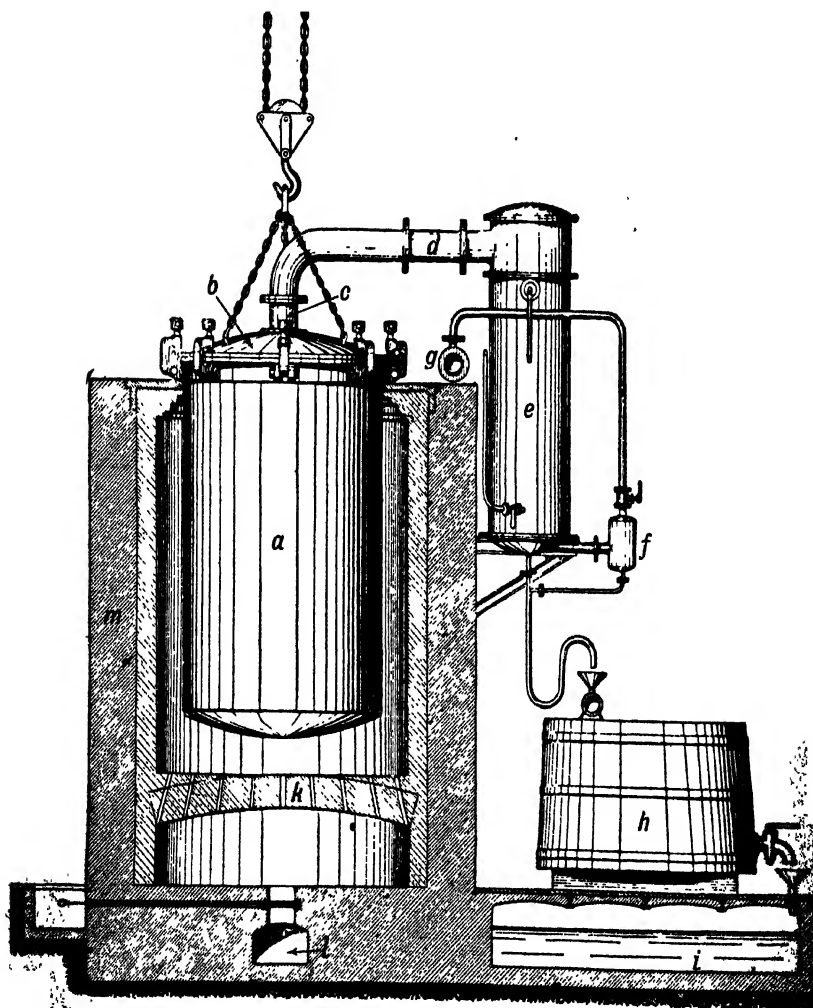


FIG. 12.—PORTABLE VERTICAL STEEL RETORT. (CAPACITY, ABOUT 5 CU. METRES.)

a, Retort; *b*, cover; *c*, outlet pipe; *d*, delivery pipe; *e*, condenser; *f*, gas-separator; *g*, non-condensable gas main; *h*, collecting vat for crude pyroligneous acid; *i*, tar-pit; *k*, perforated arch; *l*, flue; *m*, brickwork setting.

being lifted out of the oven, is lowered on to a truck which runs on rails, and the framework of which corresponds to the shape of the retort. After the charcoal has been discharged, the retort, which usually holds 5 cu. metres of wood, is run on the truck into the charging shed. Here the wood is cut up, generally by means of circular saws and splitting machines (Fig. 3, page 87), and very carefully packed in layers in the retort. The cover is then fitted, and the retort—still lying on the truck—is run to the retort-house. The ovens are arranged side by side in a row. Running above the row of ovens is a crane, which is usually electrically driven and is capable of conveying a load either in a longitudinal or transverse direction. By means of the crane, the retort is first of all lifted from the horizontal into the vertical position; it is then hoisted up and conveyed above the gangway, which runs in front of the row of ovens, to the particular oven in which it is to be inserted. By the operation of a mechanical device, movement in the transverse direction is automatically arrested as soon as the retort hangs vertically over the empty oven. The withdrawal of the retort from the oven is carried out in a similar manner. In lowering the retort, it is brought gradually from the vertical to the horizontal position, suitable precautions being taken to prevent the hot retort, or the truck which receives it, from slipping.

The remarks already made with regard to the car-retorts apply to this system also. Everything depends on the satisfactory operation of the comparatively complex transport arrangements. As long as the latter are reliable and do not require too much labour, the system must be regarded as possessing several good features.

In no other form of apparatus is the internal space so well utilised as in the vertical portable retort. This is due to the fact that the retorts are charged while cold.

Provided that the transport arrangements operate perfectly, the cost of labour for the vertical portable retorts is distinctly lower than for the small horizontal retorts (II A a).

At the same time these retorts possess certain disadvantages. For example, if the movable delivery pipes between the retorts and condensers are connected up simply by means of a socket-joint and a clay lute, leakage frequently takes place at the joint. Other and better connections are certainly available (see Fig. 12), but are apt to prove expensive owing to the

necessity of renewing the packing once or twice every day. Constant alternation in temperature causes the brickwork to crack and the retort to leak, and leads, of course, to increase in the consumption of fuel. Extra fuel is also necessary for generating the considerable amount of power required for moving, and especially lifting, the retorts by means of the crane.

In factories where no water-power is available and steam power must be used, this item is by no means negligible.

The capital cost of the installation is relatively high, owing to the necessity of providing at least a duplicate number of retorts, trucks for conveying the retorts to and from the retorts, a crane and a high retort house. Moreover, the rapid changes of temperature give rise to comparatively rapid depreciation of the ovens and retorts.

III. CARBONISING APPARATUS FOR CONTINUOUS OPERATION

All types of apparatus dealt with so far are capable of carbonising a definite quantity of wood in one single charge, which is only renewed after the process is finished. The process is therefore more or less intermittent.

We have now to consider those forms of carbonising apparatus into which the wood may be charged continuously and from which the charcoal may be removed continuously, all operations being practicable without any interruption.

A.—THE GRÖNDAL RETORT.

The completely continuous retort designed by Gröndal¹—of which, so far as the author is aware, only one example is in operation—is really a car-retort which has been developed with a view to continuous operation.

The Gröndal retort is shown diagrammatically in Fig. 13 (p. 158); on comparing the latter with Fig. 11 (page 150), the similarity is evident at once.

The Gröndal retort consists of the following main parts:—

A. A brickwork *ante-chamber*, cut off from chamber *B* and from the exterior by sliding doors, and sufficiently large to hold a car 3.5 m. long, 1.5 m. wide and 2 m. high.

¹ German patent 112,932.

B. A *pre-drying chamber*, 38 m. long, 2.6 m. high, and 1.95 m. wide, which is cut off from chambers *A* and *C* by sliding doors. The portion of this chamber adjacent to *C* is constructed of steel, and the portion adjacent to *A* of brickwork. Hot gases from the furnace *J* circulate round the steel portion and then pass into the interior of the brickwork portion, thus coming into direct contact with the wood.

C. The actual *carbonising chamber*, 26 m. long, constructed of steel and similar in cross-section to the pre-drying chamber. This chamber can be isolated from the charcoal cooler *D* and the pre-drying chamber *B* by sliding-doors which open vertically. Furnace gases circulate round the carbonising chamber, which is connected with the condenser *H* by the pipe *c*.

D. The brickwork *charcoal cooler*, 20 m. long and similar in cross-section to *C*, through which the non-condensable gases

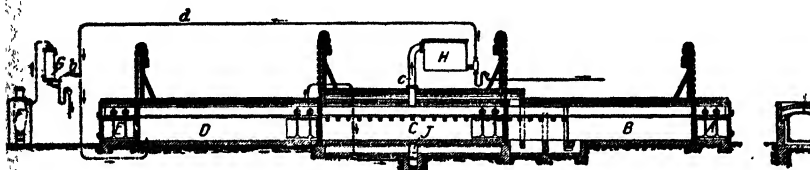


FIG. 13.—GRÖNDAL RETORT FOR CONTINUOUS OPERATION.¹

from the condenser *H* and producer-gas from *F* are conducted, before being burnt in the furnace *J*. These gases absorb heat from the charcoal and cool the latter.

E. A brickwork *chamber* which can be cut off from *D* and from the exterior by sliding doors.

F. *Producer* for generating fuel-gas from sawdust.

G. *Condenser* for removing water vapour from the producer-gas.

H. *Condenser* for the products of distillation escaping from *C*.

The wood is packed into baskets or cars which are then run into the ante-chamber *A*. If cars are used, a rail-track is laid on the floor of the apparatus; the baskets, on the other hand, are suspended from wheels which run on rails fitted on either side of the retort, as shown in Fig. 13. In each case the rails extend throughout the entire length of the apparatus.

After a basket or car has been introduced into *A*, the outer door is closed and the door between *A* and *B* is opened.

¹ German patent 112,932.

By means of a mechanical hauling arrangement the basket is then drawn into the pre-drying chamber *B*. This operation is repeated from *B* to *C*, from *C* to *D*, from *D* to *E*, and finally from *E* to the exterior. When a basket approaches one of the sliding doors an electric bell rings, giving the signal for the opening or closing of the various doors.

The wet wood thus passes from the ante-chamber *A* into the brickwork section of the pre-drier *B*, where it is exposed to the direct action of the gases from the furnace *J*; by this time, however, these gases have already given up a large portion of their heat. Passing further along the apparatus, the wood arrives in the steel section of the pre-drier, round which the hot furnace gases circulate. The next movement brings the wood into the carbonising chamber *C*. This chamber is connected with the condenser *H*, and is heated by furnace gases which pass through spiral flues. The furnace gases are derived from the furnace *J*, in which a mixture of wood-gas from *C* and producer-gas from *F* is burnt. In ordinary circumstances these gases—which should be free from oxygen—would reach the furnace *J* at the temperature of the atmosphere, owing to the cooling action of the condensers *H* and *G* respectively. In order to avoid loss of heat in this manner, the gases are preheated before combustion. This operation is carried out by connecting the pipe *b*, which conducts the cooled producer-gas from the condenser *G*, with the pipe *d* which conducts the cooled wood-gas from the condenser *H*. The gaseous mixture is then passed into the charcoal cooler *D*, through which the baskets filled with hot charcoal are being drawn. In this chamber the charcoal gives up its heat to the gaseous mixture, preheating the latter and gradually becoming cooled itself.

It must be admitted that Gröndal, in designing his retort, has very skilfully made use of the various improvements which have been introduced into the industry both recently and in the past.

To convey the wood through the different sections of his apparatus, which is 100 metres long, he employs the cars which were introduced in connection with the large horizontal retorts first used in America. He also utilises all sources of heat to the fullest possible extent.

In principle, however, the whole arrangement offers nothing new. The use of cars for continuous transport of the wood

through the carbonising apparatus and its accessory chambers, the employment of a preheater, the introduction and removal of the cars without interruption of the process, the pre-drying process, and even the details of the sliding doors, are very fully described by E. Drommart in a work published twenty years previously.¹ A German patent can only have been granted in ignorance of this publication.

Even the method of cooling the charcoal by means of non-condensable gases has been known for a long time. It was employed by Autier in a carbonising oven at Breins, near Belley, and is described in Armengaud's "*Génie industriel*," 1861.

At the same time the whole arrangement is well thought out, but the question arises as to whether the process is really capable of being carried out as smoothly as appears possible from the description given above.

The Gröndal apparatus is very similar to the car-retorts, with their accessory plant for preheating the wood, preheating the gases, and cooling the charcoal; the main difference is that the car-retorts do not permit continuous introduction of the wood and continuous removal of the charcoal.

Otherwise, the two forms of plant are practically similar even as regards performance, labour required, and capital cost.

Although the Gröndal retort has been in operation on an experimental basis since 1903, it has not yet been adopted by the industry.

The reason may be sought in the complications necessarily attaching to any apparatus in which the various operations are so entirely interdependent. An interruption occurring at any one point upsets the whole system and may bring operations to a standstill, thus creating conditions which, in a process like that of wood-distillation, are quite intolerable.

Ignition of the charcoal may take place owing to the presence of oxygen—always a possibility—in the producer-gas entering the cooling chamber; or the wood in the drying chamber may become ignited. Loss of products always results from the introduction of air into the interior of the apparatus, while the cars are being run in and out; and if the sliding doors should fail to act, the consequences would be very serious. Taking all these possibilities into consideration

¹ "*Traité de la carbonisation des Bois en Forêts*," par E. Drommart, Ingenieur civil. (Paris, J. Herzel and Co.) Page 75.

it must be admitted that continuous operation of a series of interconnected processes—namely, pre-drying the wood, carbonising the wood, cooling the charcoal, and utilising all possible sources of heat at the same time—is attended by the risk of derangements which are likely to do more than annul the advantages of the continuous process of destructive distillation.

As regards the heat economy which the process is supposed to effect, it has already been shown on page 107 that the saving which is brought about by utilising the heat stored up in the charcoal for preheating the wood-gas, and the waste heat of the furnace gases for pre-drying the wood, does not amount to even five per cent of the total quantity of heat required for the carbonisation of the wood and the subsequent treatment of the products, assuming a normal consumption of fuel.

It is questionable, therefore, whether, in order to effect a saving of less than five per cent, it is really worth while to instal large and costly plant which renders the process considerably more complicated and consequently less certain in operation.

The Gröndal retort represents a step in advance of the earlier known processes for the continuous distillation of wood, but it has yet to be decided in actual practice if the introduction of this retort has solved the problem of distillation by a continuous process.

B.—WOOD GAS-PRODUCERS.

We have now to consider another type of continuous apparatus which is more like a gas-producer, since it does not permit recovery of the charcoal; it is really a "wood gas producer" from which the volatile products of distillation are partly recovered.

The fact that charcoal cannot be recovered already determines the uses to which the apparatus can be put. A plant of this kind will never be employed for carbonising any class of wood which produces saleable charcoal, if it is at all possible to find a market for the charcoal.

The continuously operating "wood gas-producer" will therefore only be used in the following conditions:—

1. When it is impossible to sell charcoal.
2. When certain cheap kinds of wood are available, which

owing to their particular form, do not produce saleable charcoal.

The former case may be looked upon as rare, since the erection of a wood-distillation factory to operate in this manner would only be undertaken in very special circumstances.

Usually the producer will be installed to work under the latter set of conditions; that is, with rotten wood, thin branches, bark, sawdust, etc., from which more or less small or pulverulent charcoal may be expected.

These forms of raw material are capable of furnishing volatile products of distillation exactly similar to those obtainable from the parent wood.

It is preferable, therefore, not to burn them directly, but to "de-gasify" them, and then to "gasify" the residual incandescent charcoal by admitting air in sufficient quantity to generate "charcoal producer-gas."

By treating wood in producers which permit recovery of the volatile distillation products, the following are obtained:—

Wood-gas, formed by the destructive distillation of the wood as a result of the action of hot producer-gas; *producer-gas*, formed by the action of a limited quantity of air on the incandescent charcoal; *pyroligneous acid* and *wood-tar*; and finally, small quantities of *ash*.

The process really consists in destructive distillation of wood with partial admission of air, resulting in the generation of fuel-gas (in place of charcoal) and the recovery of pyroligneous acid and wood-tar, so far as the latter do not undergo combustion in the course of the process.

The simplest form of wood gas-producer (with recovery of by-products) consists of a brickwork shaft or chamber (Fig. 14) fitted near the bottom with a grate, and at the top with a cup-and-cone charging hopper which allows the wood to be introduced from time to time without interrupting the process. The gases and vapours escape at a point near the top of the apparatus and pass into the condenser.

At the beginning of the operation the lower portion is filled with charcoal which is then ignited. As soon as a sufficiently thick layer of charcoal is present, the introduction of air-dry wood is begun and carried on continuously, a regulated quantity of air being admitted at the same time.

Unfortunately, no analyses of the mixture of gas and vapour

escaping from gas-producers (with recovery of by-products) are available for the purpose of calculating the calorific power of the mixture. Hence, it is only possible to consider the action of this type of gas-producer from the theoretical standpoint, taking it for granted that the conditions are the most favourable.

We will assume that incandescent charcoal is present in

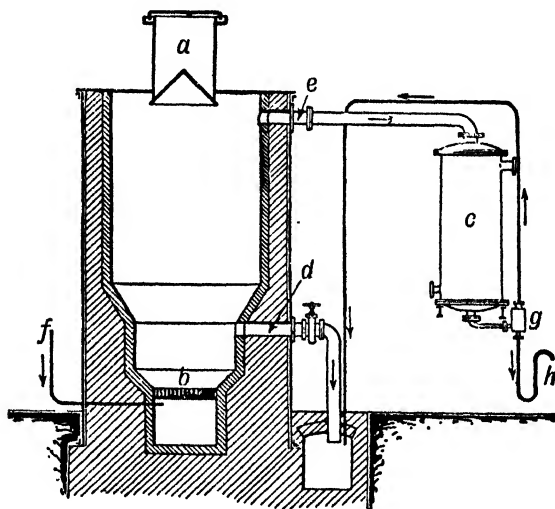
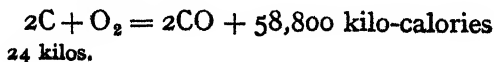


FIG. 14.—WOOD GAS-PRODUCER. A CONTINUOUSLY OPERATING STEEL CARBONISING APPARATUS, WITH ADMISSION OF AIR TO THE CHARGE.

a, cup-and-cone charging hopper; *b*, grate; *c*, condenser; *d*, lower gas outlet; *e*, upper gas outlet; *f*, air inlet; *g*, gas-separator; *h*, outflow pipe for condensed pyroligneous acid.

the lower portion of the generator, and that the carbon-content and temperature of the charge diminish from the bottom upwards. The portion of the charge lying between the layer of charcoal and the freshly introduced air-dry wood at the top consists of wood passing through all the various stages which are characteristic of the process of carbonisation.

The conversion of carbon, theoretically, into producer-gas according to the equation:—



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only takes place at a temperature of about $1000^{\circ}\text{C}.$; hence this reaction is confined to that portion of the generator which contains incandescent charcoal at that temperature.

At the same time other reactions take place, set up partly by the moisture present in the air, and partly by complex processes which so far have not been fully explained.

As a result, the gas produced by the action of limited quantities of air on charcoal contains not only carbon monoxide and nitrogen, but also carbon dioxide, hydrocarbons, hydrogen, etc.

Ebelmen¹ analysed producer-gas from charcoal and found :—

	Per cent by volume.
Nitrogen	63.4
Carbon monoxide	33.3
Carbon dioxide	0.5
Hydrogen	2.3
	} 33.8

Air-dry wood produces 25 per cent of charcoal containing 80 per cent of carbon.

Hence, 100 kilos. of air-dry wood are equivalent to 20 kilos. of carbon.

1 cu. metre of carbon monoxide (or carbon dioxide) at N.T.P. contains 0.5359 kilo. of carbon; consequently 20 kilos. of carbon correspond to $\frac{20}{0.338 \times 0.5359} = 110$ cu. metres of charcoal producer-gas possessing the composition found by Ebelmen.

110 cu. metres of producer-gas are composed of :—

	Cu. metres.	Heat of Formation. Kilo-calories.
Nitrogen	70.00	—
Carbon monoxide	36.60	$36.6 \times 1327 = +48,568$
Carbon dioxide	0.55	$0.55 \times 4334 = + 2,383$
Hydrogen	2.50	$2.5 \times 2610 = - 6,525$

The sensible heat is therefore approximately 44,500 kilo-calories. The hot gases rise from the zone of incandescent charcoal and pass through the overlying mass of wood, which is constantly being renewed. As a result, the same processes occur as in the carbonisation of wood by *direct* application of heat (hot furnace gases, etc.). "De-gasification" or destructive distillation of the wood takes place, with the

¹ "Die chemische Technologie der Brennstoffe," F. Fischer, II, p. 312.

formation of charcoal, wood-gas, pyroligneous acid and wood-tar.

To de-gasify 100 kilos. of air-dry wood, the minimum amount of heat required—deduced from practical data which only take account of the heat actually transmitted—is the following:—

6.25 kilos. of coal at 3500 kilo-calories per	
kilo. (if the efficiency=only 50%)	=21,875 kilo-calories
15 cu. metres of wood-gas at 935 kilo-	
calories per cu. metre (see p. 57)	=14,025 „
<hr/>	
Total	=35,900 „

Hence, out of the total sensible heat of the producer-gas 44,500—35,900=8600 kilo-calories remain available for other purposes.

In order that this residual heat should not be lost, it is necessary to take off the producer-gas which is formed in the charcoal zone, at two different points of the apparatus, namely:

1. From an outlet situated in the lower portion of the apparatus, where unmixed producer-gas at a high temperature is obtained.

2. From an outlet situated at the top of the apparatus. The mixture of producer-gas, wood-gas (for composition see p. 53) and vapours of pyroligneous acid and tar, passes through this outlet to the condenser, in which the last two products are condensed.

The lower gas outlet furnishes a gas possessing the composition given by Ebelmen (see above); the upper outlet, on the other hand, furnishes a mixture of this gas and wood-gas, of the following approximate composition:—

	Per cent by volume.
Nitrogen	54.0
Carbon monoxide	32.5
Carbon dioxide	10.0
Hydrogen.	2.4
Methane	0.5

These two kinds of gas, however, show very little difference in calorific value, which amounts to about 1060 kilo-calories per cu. metre in each case.

One hundred kilos. of air-dry wood produce 15 cu. metres of wood-gas (by de-gasification): hence the sum of the calorific values of the two gases represents $110 + 15 = 125 \times 1060 = 132,500$ kilo-calories. To the latter figure must be added the sensible heat of the gas taken off from the lower gas outlet, which amounts at the most to 8600 kilo-calories. The heat available from this source, however, cannot be fully utilised, since the place at which the gas is burnt always lies some distance away from the producer. In favourable conditions, therefore, de-gasification and gasification of 100 kilos. of air-dry wood result in the production of gases which are able to furnish no more than 140,000 kilo-calories, whereas the calorific value of the wood itself amounts to 300,000 kilo-calories.

It is obvious, therefore, that a wood gas-producer with recovery of the volatile distillation products is not an efficient form of heat generator, owing to the necessity of cooling the main bulk of the gas produced.

The amount of heat—140,000 kilo-calories—derived from the treatment of 100 kilos. of air-dry wood by this process must not be regarded as surplus, since a certain proportion is required in working up 45 kilos. of pyroligneous acid, produced by the above weight of wood, to acetate of lime and wood-naphtha. For this purpose 122,000 kilo-calories must be supplied; hence the actual surplus amounts to only 140,000—122,000=18,000 kilo-calories.

Again, however, this figure only holds good if the content of carbon monoxide in the producer-gas is really as high as that assumed in the above calculation, which is based on Ebelmen's figures.

Practically, therefore, the wood gas-producer only furnishes the amount of heat necessary for working up the pyroligneous acid produced, just as if the charcoal produced by the retort process were utilised to carbonise a further quantity of wood and to generate steam.

One hundred kilos. of wood furnish 300,000 kilo-calories if burnt directly, but only 140,000 kilo-calories if de-gasified and gasified according to the above process.

No products of any value are obtained when the wood is burnt directly, whereas about 75–80 per cent of the amount of volatile products normally obtainable by carbonising the wood are recovered from the gas-producer.

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Assuming that in one case the charcoal, and in the other case the producer-gas, covers the total requirements in fuel, 100 kilos. of beechwood will produce :—

Products.	By carbonisation in retorts.	By de-gasifying and gasification in a wood gas-producer.
	Shillings.	Shillings.
Acetate of lime (80 per cent)	7.5 kilos. @ 0.23 = 1.72	5.5 kilos. @ 0.23 = 1.26
Wood-naphtha (100 per cent)	1.5 kilos. @ 0.5 = 0.75	1.0 kilos. @ 0.5 = 0.50
Tar	5.0 kilos. @ 0.03 = 0.15	4.0 kilos. @ 0.03 = 0.12
	2.62	1.88

According to experience, the total costs (consumption of lime, wages, management, depreciation, maintenance, etc.) for the carbonisation of 100 kilos. of air-dry wood in large retorts, and treatment of the distillate for acetate of lime (80 per cent), wood-naphtha and tar, amount to about 1.5 shillings. If we assume that, owing to the lower capital cost and the smaller amount of labour required, the expenses for the gas-producer only amount to two-thirds of this sum—namely, one shilling—and also that the cost of 100 kilos. of wood is no more than 0.5 shilling—the price of sawdust—then the financial details of retort process and gas-producer process compare as follows, per 100 kilos. of air-dry wood :—

	Retort Process.	Producer Process.
	Shillings.	Shillings.
Costs	1.5	1.00
Wood	0.5	0.50
Expenditure	2.00	1.50
Income	2.62	1.88
Difference	0.62	0.38

The figures for the producer will be somewhat more favourable if we assume that the amounts of acetic acid, naphtha and tar representing the difference between the yields from the retort and those from the producer have been utilised by

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combustion in the producer. The following quantities of heat would be derived from this source :—

	Kilo-calories.
1·2 kilos. of acetic acid at 3505 kilo-calories	= 4,200
0·5 kilo. of wood-naphtha at 5307 kilo-calories	= 2,650
1·0 kilo. of tar at 8000 kilo-calories	= 8,000

Total = 14,850

Even if we add to this figure the 8600 kilo-calories representing the sensible heat of the gas issuing from the lower gas outlet, the total gain is only about 23,500 kilo-calories in the most favourable circumstances. With air-dry wood at 0·5 shilling per 100 kilos. the money-value of this gain is only 0·04 shilling—a quite insignificant sum.

These figures show that wood gas-producers can never be regarded as free sources of heat for generating steam—a claim that is often made. The steam is only generated by sacrificing the total production of charcoal and about 25 per cent. of the possible yields of acetic acid, wood-naphtha and tar; the price, therefore, is dear enough, especially as the total amount of steam which can be generated is very little more than the amount required for working up the pyroligneous acid obtained from the producer.

As long as the wood is capable of carbonisation in some form of retort, it will be found more profitable to adopt the retort process—even if the charcoal is employed as fuel—than to treat the wood in a gas-producer with recovery of by-products and consequent cooling of the main bulk of the gas.

In view of the above figures, which always tend to favour the gas-producer, the author is of opinion that only in certain special conditions can the producer process be adopted with advantage. It may be employed to utilise the very cheapest forms of waste material, such as sawdust, residues from extraction processes, etc., which cannot be carbonised at a profit in retorts of any design whatsoever; or, in cases where the charcoal is unsaleable or can only be burnt with difficulty.

CHAPTER XII

CARBONISING APPARATUS FOR THE TREATMENT OF PULVERULENT, GRANULAR AND SMALL WASTE DERIVED FROM WOOD OR OTHER CELLULOSIC MATERIAL

THIS class of raw material comprises all kinds of amorphous waste wood, such as sawdust, shavings, raspings and turnings, which result from the mechanical treatment of timber; also the waste material of other industries, for example, the extracted stones, or "grignons," which form the residue in the manufacture of olive oil.

As a general rule the composition of these forms of waste wood is similar to that of the parent wood, provided that no chemical action has taken place in the meantime. At any rate, this holds good for the various kinds of waste which are obtained as a result of the mechanical treatment of hardwood timber.

Softwood waste, on the other hand, exhibits certain differences. The parent wood always contains a certain amount of terpenes (oil of turpentine), but these substances, which are highly volatile, can no longer be detected in the sawdust and shavings, since they are driven off completely by the heat evolved and the draught of air set up during the operation of sawing the wood.

For this reason, sawdust and shavings from softwood are quite unsuitable material for the production of oil of turpentine, although the latter may be present in the parent wood.

Disregard of this fact has already ruined many schemes which, on paper, appeared to be highly lucrative. In this connection it is only necessary to recall the famous bankruptcy of the "Trebertrocknungsgesellschaft" of Cassel, which squandered over four million pounds within five years.

in attempting to utilise the amorphous wood-waste of saw-mills by destructive distillation.

Wood-waste is usually employed directly as fuel at the place where it is produced; and this is probably the most rational method of utilisation, especially since the recent introduction—particularly in the United States and Sweden—of continuous sawdust furnaces. The sawdust is either burnt directly on rotary grates, etc., or else it is used for the generation of fuel-gas in a special form of producer. The gas is passed through a condenser, which removes most of the water vapour, and it can then be burnt in the furnace.

In some cases the sawdust producer is combined with a coke producer, the object being to make use of the water vapour, which always accompanies the wood-gas in fairly large quantities, for generating a species of water-gas.

Enormous heaps of sawdust gradually accumulate round the larger sawmills, especially in America and Sweden, in spite of the fact that a considerable quantity is used to generate heat and power, and the only method of removing it is to burn it in the open.¹

Obviously, these conditions, which are the same in practically all countries, must render sawdust in certain localities very cheap raw material for destructive distillation; hence, it is not surprising that during a long period frequent attempts have been made to utilise sawdust in this way.

The patent literature of the various countries contains descriptions of every conceivable form of carbonising apparatus for the treatment of amorphous wood-waste, but only a few factories exist in which one or other of these processes may be found in actual operation, apart from experimental installations run on more or less large-scale lines.

The destructive distillation of sawdust has always been the subject of experiment and still is, in spite of the disastrous experience of the "Trebertrocknungsgesellschaft."

Various factors have proved, up to the present, serious obstacles to the successful utilisation of this cheap form of raw material.

One of the most important of these factors is the powdery nature of the resulting charcoal.

¹ The use of sawdust as a fuel—either directly, or indirectly as producer-gas—does not fall within the scope of this book. Information on the subject may be found in Hubbard's "Utilisation of Wood Waste" (London, 1920, Scott, Greenwood and Son.)

The consumption of charcoal in this particular form is relatively small. This is a serious disadvantage in view of the fact that a sawdust distillation plant must be capable of large output, otherwise no undertaking of the kind can hope to show a profit.

Even if the excess of charcoal, over and above the amount which can be sold, is converted into briquettes, the position is not altered very greatly. The demand for charcoal briquettes is only small, and a single factory would be sufficient to meet the requirements of a whole country.

In these conditions the only alternative is to utilise the excess of charcoal as fuel. If this plan be adopted it is likely to upset commercial calculations, since a factory could only be run on these lines in specially favourable local conditions.

Apart from the difficulty in regard to the charcoal, the relatively low yields of acetate of lime and wood-naphtha obtained by carbonising sawdust form a serious disadvantage.

In practically every country the largest proportion of sawmill waste is derived from softwood.

Softwood, however, usually gives only 50 per cent of the yields of acetate of lime and wood-naphtha obtainable from an equal weight of hardwood.

When softwood is carbonised in the form of billets, this deficiency is balanced by the production of the valuable pine-oil, the sale of which compensates in a great measure for the lower revenue from acetate of lime and wood-naphtha. It is impossible, however, to obtain pine-oil by the carbonisation of softwood sawdust.

The working costs—referred to the same unit—for the treatment of sawdust and of an equal quantity of billet-wood, or any form of wood capable of producing saleable charcoal, are about equal. Consequently, except under particularly favourable local conditions, it is impossible—as a very simple calculation will show—to derive any profit from the carbonisation of *softwood* sawdust as long as it is necessary to utilise the residual powdery charcoal as fuel in the plant itself.

Apart from obstacles of a purely commercial character, the process of carbonising powdery and bulky waste material, such as sawdust, offers certain technical difficulties which up to the present have only been partially overcome.

If the wood is in powdery form, the particles lie packed together much more closely than if the wood is in larger

pieces. Close packing hinders circulation of the gaseous products and prevents the latter from acting as carriers of heat.

In these conditions, transmission of heat to the material undergoing carbonisation is effected almost exclusively by conduction and radiation from the heated surfaces of the container; it is useless, therefore, to employ carbonising apparatus of large diameter. If attempts are made to carbonise sawdust in apparatus used normally for billet-wood, it is found that the process cannot be carried out in a reasonable length of time. An insulating layer of charcoal forms in the neighbourhood of the heated surface of the container, and hinders further penetration of heat. In addition, evolution of the gaseous products is retarded, owing to the absence, inside the mass, of sufficiently large channels for escape.

Hence, it is only practicable to carbonise the various kinds of small waste material mentioned above, by employing one of the following methods:—

1. The material is compressed into briquettes before carbonisation.¹

2. Stationary retorts fitted with stirring apparatus, rotary retorts, or rotary retorts fitted with stirring apparatus are employed, with the object of facilitating the transmission of heat from the walls of the retort to the material.

3. Carbonisation of the material in thin layers.

The object of the processes included under (1) was to produce solid blocks of wood by briquetting the amorphous waste before carbonisation. It was believed that these briquettes, when packed into the retort in layers, would behave like billet-wood and leave a sufficient number of channels both for the conduction of heat and for the escape of the gaseous products; and further, that these processes would furnish charcoal in the form of lumps—just like billet-wood charcoal—instead of in the powdery form. This principle formed the basis of the notorious Bergmann patents adopted by the “Trebertrocknungsgesellschaft.” The advantages expected from the briquetting process were never realised, for the briquettes fell to pieces either during the process of car-

¹ Heidenstamm, German patents	65,447; 80,624; 88,014.
Bergmann	100,414; 103,922; 114,551.
Heimsoth	74,511.
Katz	90,801.

bonisation or afterwards ; moreover, owing to the close texture of the compressed material, the temperature required for carbonisation was so high that the retorts were burnt through in a short time, and the charcoal burnt with difficulty and was graphitic in character.

This method (1) of treating sawdust is now obsolete;¹ it failed both to render carbonisation of this class of material a practicable process and to achieve its final object—the production of charcoal in lump form.

Method (2) covers a series of processes which at first sight would appear to offer the correct solution of the problem.

Sawdust and most of the other forms of small waste material are bulky. A factory must be capable of treating large quantities of these materials, since a small installation can never pay ; in consequence, it is necessary to provide for the movement of large volumes of relatively low weight, and in these conditions only a continuous process of carbonisation appears to be suitable.

Halliday,² of Salford, was the first to adopt this method. His apparatus consisted of a number of horizontal superimposed cast-iron cylinders connected alternately with one another. A screw or worm revolved in each cylinder, keeping the material in constant agitation and gradually moving it forward. The charcoal was eventually delivered into a tank of water. The cylinder was heated in the same manner as the horizontal retorts, and the rate of movement of the screw was so adjusted that the wood remained for a certain definite time in the cylinder.

It is a well-known fact that sawdust, especially when derived from floated wood (see p. 32), contains a considerable quantity of moisture, which renders the period of carbonisation unnecessarily long, reduces the yields, and causes a very marked increase in the consumption of fuel ; moreover, it dilutes the pyroligneous acid, with the result that costs of evaporation are increased.

With the object of avoiding these difficulties, Ekelund³ and Knopf⁴ introduced certain improvements into the Halliday process. Several superimposed cylinders were operated as one

¹ See chap. xxi.

² See Repertory of Patent-Inventions, October, 1849, p. 213.

The Halliday process is also described in detail in Muspratt's "Chemistry," Vol. 1, p. 23.

³ German patent 77,368.

⁴ German patent 106,714.

system ; the lowest cylinder was exposed to the full heat of the furnace, whereas the top cylinder was only heated by the waste furnace gases. The sawdust was fed continuously into the top cylinder, where the greater part of the moisture was expelled and conducted off separately. The material, by this time sufficiently dry, then ran downwards into the next cylinder and so on from cylinder to cylinder. The process of carbonisation was thus rendered continuous, and finally the charcoal was removed continuously from the bottom cylinder.

Saulmann¹ and Larsen² employed rotary retorts instead of agitating apparatus, and abandoned the idea of continuous operation.

P. Schneider³ introduced agitating apparatus into rotary retorts and was thus able to secure the advantage of highly uniform heating, as offered by that type of retort, and at the same time the advantages of continuous operation.

Halliday's retorts were used in England for carbonising sawdust, spent bark from tanyards and extracted dye-woods. Larsen rotary retorts are still used in a Belgian factory for carbonising quebracho waste, and Schneider's retort was worked for a considerable period on an experimental scale in a German factory which has since gone bankrupt.

Continuous carbonisation of sawdust and similar waste materials by means of the various forms of plant included under (2) may appear simple, but in practice considerable difficulties are experienced in keeping the process running with regularity and certainty, as the author observed in the case of an experimental installation erected to operate Schneider's process. In this process the sawdust or shavings were fed, by means of an elevator, into a pre-drier around which waste gases from the retort furnace were conducted ; thence, the dried material ran down into the retort itself. The retort was made of cast-iron and rotated between two stationary end plates which were held tight against the retort by springs ; one plate contained an opening through which the raw material entered the retort ; and the other plate was fitted with outlets for the charcoal and volatile products of distillation respectively.

Inside the retort was an agitating apparatus which was

¹ German patents 112,178 ; 112,398.

² German patent 113,024.

³ German patents 107,224 ; 132,679.

fitted with blades, like a ship's propeller, and rotated in the opposite direction to the retort.

The charcoal left the retort by the lower of the two outlets, and entered a closed trough which contained spiral conveyers and lay in an outer cooling trough. By means of this arrangement, which worked exactly as foreseen in the patent specifications, the charcoal was taken up as it came from the retorts, cooled, and delivered into iron containers.

The distillation products were drawn off by means of a fan placed at the end of the condenser ; after leaving the retorts these products passed into a dust-catcher and thence into the condenser. The non-condensable gases were returned to the furnace by the action of the fan.

Although the plant worked very well for a time, it exhibited the weaknesses inherent in all mechanism which is subjected to high temperatures. As a result of unequal expansion and insufficient lubrication (a very difficult operation to carry out at the temperature employed) friction was set up, which caused the driving belts to slip off and gave rise to fracture of the driving mechanism, axles, certain parts of the agitators, etc. In short, with such complicated and inter-dependent arrangements there are always numerous possibilities of breakdown.

Accidental stoppage or inefficient action of the elevator conveying the raw material may lead to the retort running empty. In these conditions the retort readily becomes overheated, with the result that further trouble may arise, quite apart from the losses caused by influx of air, which increases greatly if the supply of raw material is interrupted while the retort is running.

On paper, continuous carbonisation, by means of the various mechanical retorts described above, may appear to be a simple matter, but in practice the process offers great difficulties in so far as smooth and regular operation for an unlimited period is concerned.

Apart from the purely commercial question of profit, it is mainly owing to these difficulties that hitherto the various forms of mechanical apparatus have seldom advanced beyond the experimental stage.

Rotary retorts certainly offer fewer difficulties of this kind, but they can only be operated intermittently—a feature which distinctly limits their application.

Another serious disadvantage attaching to all mechanical retorts or retorts fitted with internal mechanism is the formation of fine dust, owing to constant agitation of the powdery charcoal. This dust finds its way into the condensers and thence into the condensed liquor, thus contaminating both the pyroligneous acid and the tar.

It is essential, therefore, to instal efficient dust-catchers—preferably of the self-emptying type—between the retorts and condensers, but as a rule it is found that these contrivances give rise to trouble and loss.

It may be stated briefly that no form of apparatus, included under (2), which has been introduced up to the present can claim to be perfect or even reliable and regular in operation.

Group (3) comprises the various forms of apparatus which are designed to carbonise small waste material in thin layers.

The simplest form of plant employed for this purpose is similar in principle to the acetone retort shown in Fig. 45. The waste material is spread out in a thin layer on plates or trays which are arranged in tiers on an iron car. The latter is then run into a horizontal retort, or suspended in a vertical retort. Large-scale trials, conducted by the author, showed that this method of carbonisation gives very good results as far as the products are concerned, but the loading of the trays requires much hand labour, and owing to operation being intermittent and the voluminous nature of the material, the performance of the plant is not very great.

In spite of these disadvantages, plant designed on the above lines can be trusted to operate with absolute certainty and regularity for an unlimited period, but it is unsuitable for dealing with very large quantities of the raw material.

The principle of distillation in thin layers is also employed in certain forms of vertical carbonising apparatus, which are copies of the plant used in the Thuringian mining industry for distilling lignite.

The apparatus consists of a vertical cylindrical chamber, constructed of steel or brickwork (Fig. 15). Inside the chamber is a column built up of superimposed, conical cast-iron rings which overlap like the laths of a Venetian blind. Between the wall of the cylinder and the column is an annular space, 10–15 cm. across, which, during the process, is occupied by the material undergoing carbonisation. The furnace is situated at the base of the cylinder and the furnace gases pass through a

spiral flue which encircles the cylinder. The raw material, which must not be too finely divided, is fed into the cylinder from above, by means of a cup-and-cone charging hopper; it travels downwards gradually in the space between the wall of the cylinder and the column. The material in the course of its descent is subjected to steadily increasing temperatures,

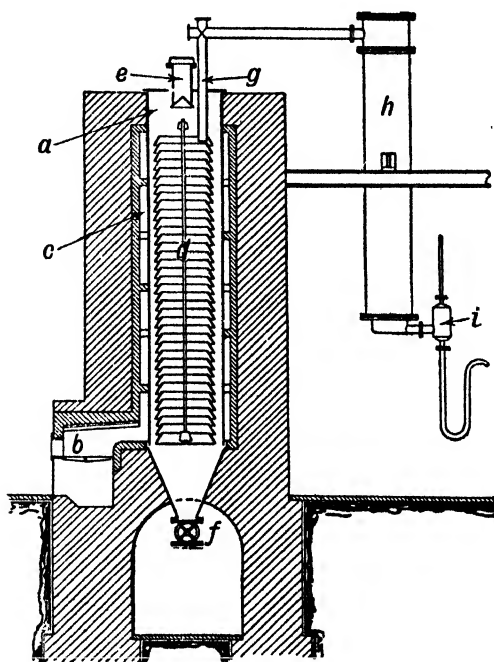


FIG. 15.—CONTINUOUS CARBONISING APPARATUS SUITABLE FOR THE DENSER KINDS OF SMALL WASTE MATERIAL.

a, Wall of cylinder; *b*, furnace; *c*, spiral flue; *d*, column of cast-iron rings; *e*, charging hopper; *f*, rotary valve; *g*, outlet pipe for volatile products; *h*, condenser; *i*, gas-separator.

and passes through all the phases of carbonisation; finally, it is discharged as charcoal through an airtight rotary valve at the bottom of the apparatus.

The volatile products of distillation escape through the annular openings between the conical rings of the column into the vapour outlet pipe, which is usually fitted to the uppermost ring, the latter being closed at the top.

This type of apparatus has proved particularly well adapted for the carbonisation of lignite; it can be employed equally well for any small waste material which is not too light and bulky and by virtue of its own gravity is able to travel gradually to the bottom of the apparatus.

An example of such material is the residue, or so-called "grignons," obtained in the manufacture of olive oil. The yields resulting from the destructive distillation of this material are given on page 37.

Quebracho chips and other extraction residues can also be carbonised satisfactorily in this form of apparatus.

Another form of plant which carbonises small waste material in thin layers is the *continuous mechanical retort* employed in certain parts of England and Scotland.

Several different forms of this type of plant are in operation. One form consists of an oblong steel chamber, set in brickwork and heated externally by furnace- or producer-gases. The chamber is divided horizontally across the middle by a steel plate. At each end of the chamber are drums, which are rotated by some form of power and carry endless chains fitted with a series of scrapers. The material is fed in continuously from above, through a hopper situated at one end of the retort and fitted with a rotary valve. The material falls on to the middle plate, along which it is conveyed by the action of the scrapers to the opposite end of the retort. Here, it falls on to the bottom of the retort and is gradually conveyed to the charging end again, where it is discharged continuously, as charcoal, through a rotary valve into iron cooling boxes, or into a cooling trough fitted with a conveyer screw (see p. 175). The volatile products are usually taken off at the top of the retort, and pass to the condenser in the usual manner.

The operation of these retorts is fairly satisfactory, but the mechanism is somewhat complicated and shows the tendency to break down which is common to all apparatus containing moving parts subjected continually to relatively high temperatures; in consequence, the cost of maintenance is often excessive. Another disadvantage is the difficulty of avoiding influx of air, which causes a considerable reduction in the yield of wood-naphtha.

In Great Britain this type of retort is used chiefly to carbonise the turnings and chippings obtained in the manufacture of bobbins for the textile industry. This material

consists mostly of birch- and beechwood which is thoroughly seasoned before use and therefore contains only a relatively small percentage of moisture. It produces a high-class quality of "flake" charcoal, which is used for chemical purposes, as an insulating medium in refrigerator plant and also, in certain cases, for the manufacture of a special type of briquette for use in laundry-irons. During recent years the supplies of raw material have become considerably reduced, for several reasons, and only a small number of these retorts is now in operation.

A vertical mechanical retort which possesses certain features of interest has recently been introduced by Ross and Corner.¹

According to the patent specification this apparatus consists of a vertical cylindrical chamber, constructed of cast-iron or other suitable material, and heated externally. The cylinder is fitted with a series of trays, each of which contains a slot or opening through which the material undergoing carbonisation can fall to the next lower tray. These openings are so arranged that the material, after falling on to any particular tray, must travel practically right round the tray before reaching the next opening. A vertical shaft passes through the cylinder and carries a series of arms which extend horizontally over the trays. Blades of varying width are attached to the arms, and serve to spread the material over the trays. The first blade, which comes into contact with a freshly fallen heap, scrapes off a thin layer; the next blade, which is somewhat wider, scrapes off a further layer; and so on, the material becoming spread in this way over the whole surface of the plate and thoroughly agitated. Finally, the last blade, which only just clears the trays, scrapes the whole of the material to the slot, down which it falls to the next tray, where the process is repeated. During its passage from the top of the apparatus to the bottom, the material is therefore obliged to travel a relatively great distance. A circular hole is cut out of each tray, large enough to take the central shaft and to leave an annular space, up which the volatile products escape to the top of the apparatus; here they are taken off through an outlet in the cover. The material is fed in at the top by means of a conveyer screw and a rotary valve.

The charcoal is taken off at the bottom of the apparatus, which ends in a cone fitted with a rotary valve.

¹ Brit. Patent 118,960 (New Series, 1917). Blair, Campbell and McLean, Ltd., J. K. Ross and E. P. Corner.

Any suitable form of power may be used to rotate the arms ; the speed of rotation must be so adjusted as to ensure thorough carbonisation of the material.

We have seen that, for the carbonisation of billet-wood, slabs, laths, and "smalls" exceeding a certain size, numerous types of plant are available, which have been thoroughly tested in practice and are quite reliable in operation ; carbonisation of small waste, on the other hand, has not yet emerged from the experimental stage.

It is now generally recognised that the carbonisation of small waste, in spite of its low cost, seldom gives the financial results obtainable from block-wood ; at the same time it is possible in certain conditions to operate the former process with a reasonable degree of success, even if the huge returns promised by many inventors fail to be realised.

Continuous progress is being made in the design of plant for the efficient carbonisation of small waste material, and the prospects of the process tend to improve accordingly.¹

¹ Descriptions of other forms of carbonising apparatus for small waste material will be found in Hubbard's "Utilisation of Wood Waste." See also chap. xxi.

CHAPTER XIII

ARRANGEMENTS FOR CONDENSING AND COOLING THE VOLATILE PRODUCTS OF DISTILLATION

ON page 104 it was shown that for every 100 kilos. of air-dry wood carbonised, the following quantities of heat passed from the carbonising apparatus to the condenser, provided that the charge of wood was heated on the *indirect* principle :—

35,250 kilo-calories, derived from 50 kilos. of pyroligneous acid and tar vapours heated to 300° C. (pyroligneous acid reckoned as water).

1,610 kilo-calories from the wood-gas (reckoned as air).

Total=36,860 kilo-calories per 100 kilos. of air-dry wood.

It is assumed that the condensed liquor and the non-condensable gas leave the condenser at a temperature of 20° C.

If the initial temperature of the vapour-gas mixture entering the condenser is 300° C. and the exit temperature of the condensed liquor and non-condensable gases is 20° C.; and if the initial temperature of the cooling water is 15° C. and the final temperature 50° C., then, according to Hausbrand,¹ the mean temperature difference between the cooling agent and the mixture of gas and vapour amounts to about 60°. The coefficient of transmission of heat from vapours to water in motion, through metal partitions, is about 1000 kilo-calories per hour, for 1 square metre of cooling surface and a temperature difference of 1° C.—making allowance for all the conditions of practical operation; for gases under the same conditions the coefficient is only about 20 kilo-calories. The coefficient of transmission to *air* is likewise only 20 kilo-calories for both vapours and gases.

If *air-condensers* are employed, 100 kilos. of wood carbonised hourly will require a cooling-surface of $\frac{36,860}{60 \times 20} = 30.71$ sq.

¹ Hausbrand: "Verdampfen, Kondensieren und Kühlen" (Berlin, 1909), p. 8.

metres, assuming that the heat is transferred to the condensers at a perfectly uniform rate.

With *water-condensers*, on the other hand, the area of cooling surface required is

$$\frac{35,250}{60 \times 1000} = 0.59 \text{ sq. metres for the vapours.}$$

$$\frac{1,610}{60 \times 20} = 1.34 \quad \text{,,} \quad \text{,,} \quad \text{non-condensable gas.}$$

$$\text{Total} = 1.93 \text{ sq. metres.}$$

These figures clearly demonstrate that air-condensers must prove considerably dearer than water-condensers, more especially in view of the fact that, owing to the comparatively rapid action of dilute acetic acid on steel or wrought iron, air-condensers must always be constructed of copper.

As a matter of fact, water is practically always employed as the cooling agent in the wood-distillation industry. Air-cooling is only adopted in quite exceptional circumstances.

The above figures, however, do not agree with the actual requirements of practice, but only apply if the amount of heat (see above) enters the condensers at a uniform rate throughout the whole period of carbonisation. This is not the case, as we have already seen, for at certain stages of the distillation process violent evolution of gas occurs, and during this period the rate at which heat is transferred to the condenser must be correspondingly greater. Since the amount of heat which must be dealt with during the violent phase of distillation varies greatly, according to the form of carbonising apparatus employed, the size of the charge and the kind of wood, it is impossible to determine theoretically the dimensions necessary for a condenser. Here again, practical experience is the only reliable guide.

In view of the violent phase of carbonisation it is necessary to provide greater cooling surfaces than are required during the remainder of the process; consequently, the capital cost of a wood-distillation plant is increased without adequate return.

This objection has been overcome by adopting a centralised system of condensation—as for the American kilns (Fig. 5, p. 132)—and so arranging operations that the individual carbonising plants connected with the central condensing plant are all at different stages of the process; in these

conditions the violent phase of carbonisation is of very little, if any, importance.

It has already been mentioned that when carbonising apparatus is fitted with top gas-outlets the volatile products leave the apparatus at a comparatively high temperature, and that consequently there is a tendency for the connecting pipes between the carbonising apparatus and the condenser to become choked with tar-coke. The longer the connecting pipes, the greater is the danger of coking.

If retorts fitted with top gas-outlets are worked with a central condenser plant, it is impossible to avoid long connecting pipes and consequent formation of tar-coke; the pipes must therefore be cleaned frequently.

This disadvantage may be minimised to a certain extent, but it is impossible to eliminate it entirely; moreover, the use of a central condenser system renders it difficult to keep the operation of each individual carbonising plant under observation. For these reasons, separate condensers for each apparatus, though more expensive, have usually been employed hitherto in preference to the cheaper central condenser system.

In the case of kilns fitted with bottom outlets the volatile products of carbonisation leave the apparatus at a comparatively low temperature which involves no danger of the formation of tar-coke. Consequently, a central condenser system is almost invariably adopted for that type of plant.

We have now to consider the design and construction of the various forms of condensing and cooling apparatus.

Experience has shown that copper is the only suitable material for the construction of cooling surfaces which come into contact with acetic acid vapour.

Owing to the nature of the vapours and gases entering the condensers, there is a tendency for the cooling surfaces to become encrusted with tarry matter; it is essential, therefore, that the condenser be easily cleaned.

For this reason it is customary to pass the mixture of gas and vapour *through* copper tubes, and to allow the cooling water to circulate *round* the tubes.

If, on the other hand, the cooling water readily deposits a large amount of scale, or if the condenser is dealing with the volatile products from kilns, which show little tendency to form deposits on the tubes, or again, if the patent tar-separator¹

¹ German patent 189,303.

is employed, it is usual to pass the cooling water through the tubes and to circulate the products round them.

These condensers may be of the self-contained types—clearly illustrated in Figs. 16 and 17—which are disposed either horizontally or vertically; or they may consist of a bundle of parallel tubes, fitted at either end with copper chambers carrying the necessary inlet and outlet pipes, and completely immersed in a wooden or iron water-tank.

By removing the covers of the inlet and outlet chambers every tube is exposed and can be easily cleaned with brushes, etc.

The ease with which the tubular type of condenser can be cleaned is a distinct advantage, but the cooling effect is only satisfactory if the cooling surface is relatively large.

The length of the tubes must be limited in order to facilitate cleaning and to avoid sagging, etc.; the cooling path is therefore relatively short and in consequence the cooling effect is less than that of a coil condenser (Fig. 18) of equal size.

In the tubular condensers (Figs. 16 and 17) the main stream of gas and vapour is split up into as many separate streams as

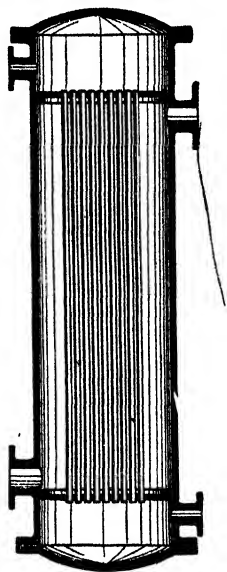


FIG. 16.—VERTICAL TUBULAR CONDENSER.

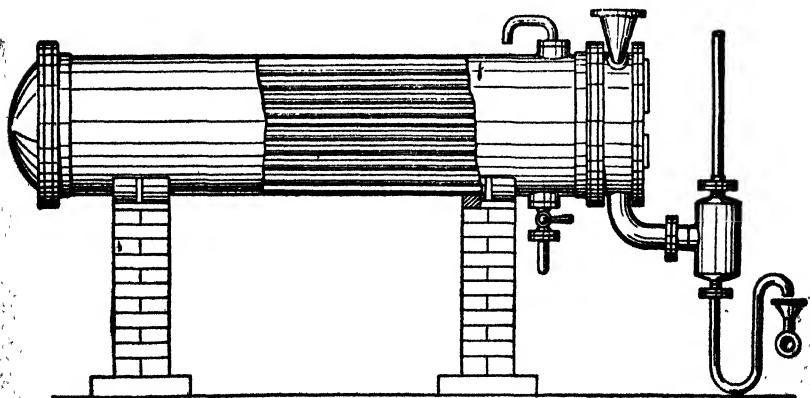


FIG. 17.—HORIZONTAL TUBULAR CONDENSER.

there are parallel tubes, but in the coil or worm condenser the gaseous mixture passes through a single tube which, in order to afford an equal area of cooling surface, must be correspondingly longer; this accounts for the better cooling effect exhibited by the coil condenser (Fig. 18) per unit of cooling-surface area.

In order to facilitate cleaning, the tube forming the coil condenser is not wound into a spiral, but is made up of a

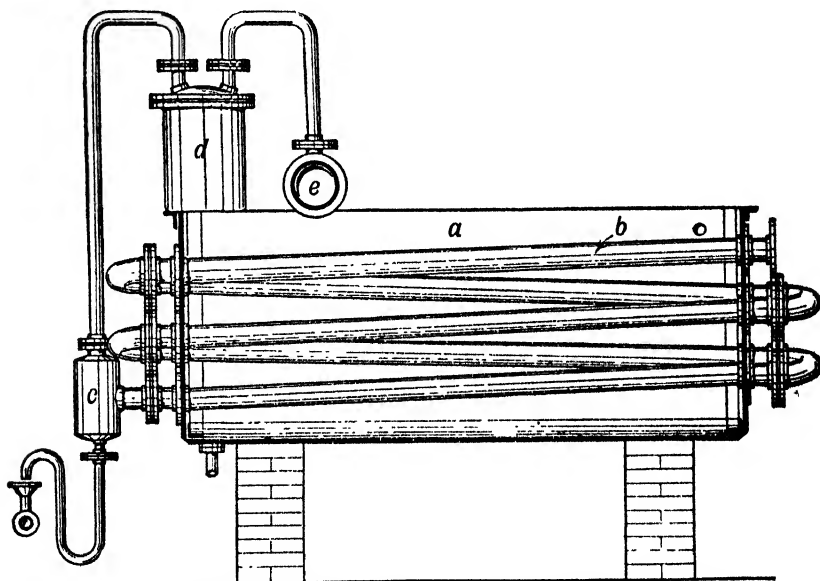


FIG. 18.—COIL CONDENSER, COMPOSED OF STRAIGHT TUBES AND ELBOWS.

a, water-tank; *b*, copper condenser-tube; *c*, gas-separator; *d*, hydraulic seal; *e*, gas-main.

number of inclined and superimposed straight tubes which are connected by means of bends or elbows. The connecting elbows lie outside the water-tank, and on removing them each separate condenser tube can be easily cleaned. Fig. 18 shows this form of coil condenser, which is the one most generally used.

If greater capacity is required, several of these coils, each lying in a vertical plane, are arranged in a single large water-tank and are connected in parallel, at one end to the main

vapour delivery-pipe and at the other end to a corresponding outlet pipe.

As mentioned above, it is always the custom to employ a central condenser system for the American kilns. This system

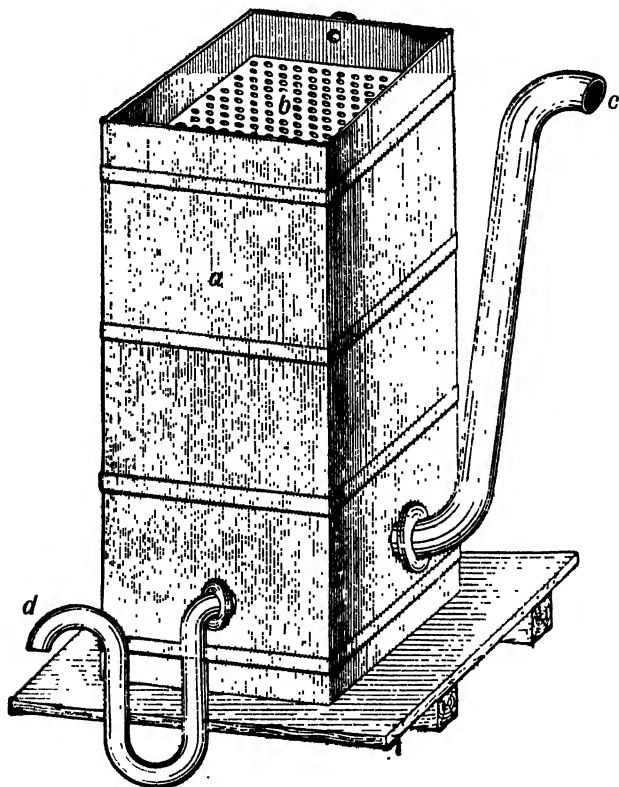


FIG. 19.—AMERICAN TUBULAR CONDENSER; VAPOUR CHAMBER OF WOOD, COOLING TUBES OF COPPER.

a, wooden tank; *b*, wooden tube-plate; *c*, vapour inlet-pipe; *d*, condensed liquor outlet-pipe.

is composed of a number of condensers, one of which is shown in Fig. 19. Each separate condenser consists of a rectangular wooden tank, fitted at a short distance from either end with two horizontal perforated wooden partitions between which the copper condenser-tubes extend. The tubes are fitted into the perforations with the aid of a tube expander, like the

tubes of a locomotive boiler. The mixture of gas and vapour enters the condenser immediately above the lower tube-plate and circulates round the tubes, finally escaping through an outlet beneath the upper tube-plate and entering an adjacent condenser. The cooling water, on the other hand, flows through the tubes. Owing to the action of the suction fans at the end of the system, the pressure prevailing in the space between the tube-plates is somewhat below that of the atmosphere;

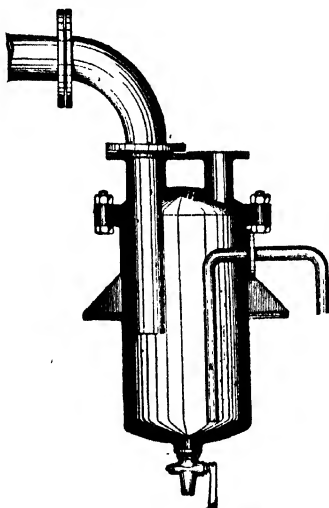


FIG. 20.—DEVICE FOR SEPARATING WOOD-GAS
AND PYROLIGNEOUS ACID.

hence there is no danger of loss by leakage through bad joints. The condensed liquor flows away continuously through a siphon pipe.

Condensers of this type are certainly cheap to construct, but, as mentioned above, they should only be used if the volatile products from the carbonising apparatus have already become cooled to such an extent—possibly as a result of passing through a long connecting pipe—that deposition of tar-coke in the condenser itself is no longer possible.

When a separate condenser is employed, a copper vessel fitted with a siphon run-off is often placed between the carbonising apparatus and the condenser, with the object of

separating a certain amount of tar before the volatile products enter the condenser. With this arrangement it is found that only a small amount of tarry deposit is formed in the con-

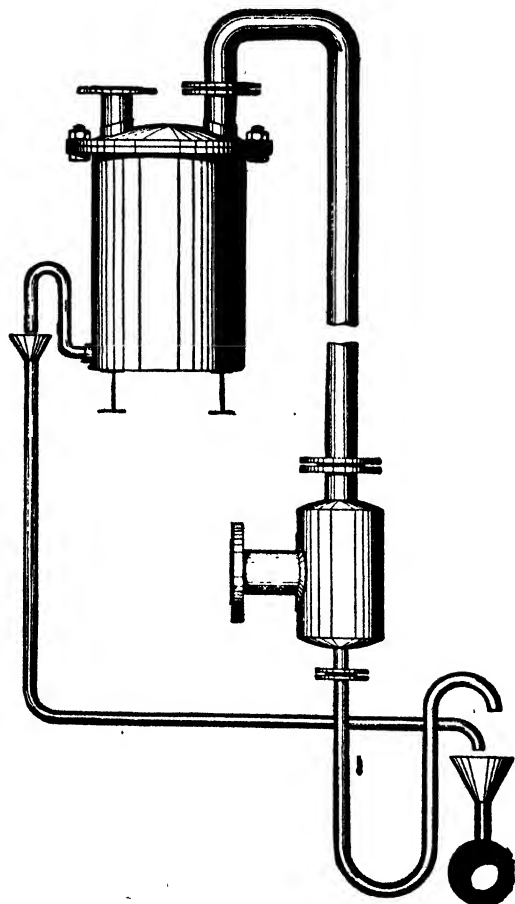


FIG. 21.—DEVICE FOR SEPARATING WOOD-GAS AND PYROLIGNEOUS ACID.

denser; cleaning is less frequently required, and above all is very easily carried out, owing to the less objectionable nature of the deposit. The condensed liquor, consisting of a mixture of tar and pyroligneous acid, obtained in a tar-

separator of this type, is returned to the main bulk of the distillate coming from the condensers.

The advantages gained by the use of these tar-separators are nullified to a certain extent by their tendency to become stopped up, owing to the formation of tar-coke.

The condenser outlet always discharges into some form of apparatus which brings about the separation of wood-gas and condensed liquor, and allows the flow of the latter to be observed. This arrangement is also provided with a hydraulic seal for the purpose of preventing direct connection between the carbonising apparatus and the central gas-main. In the apparatus shown in Fig. 20 the hydraulic seal and the gas-separator are combined; in that shown in Fig. 21 they are separated.

CHAPTER XIV

TREATMENT OF THE WOOD-GAS

THE composition, yield, properties, etc., of the non-condensable wood-gas have already been discussed in detail in Chapter V.

In Chapter XIII we have seen that it is usual to provide each separate carbonising apparatus with condensers for dealing with the vapours and non-condensable gas. Scrubbing of the gases, however—no matter whether they are intended for heating or for power purposes—is always carried out—and quite rightly so—in a central plant. In Chapter III it was mentioned that, during the violent phase of carbonisation, gases possessing very high calorific value (hydrocarbons) were evolved in large quantities. During this period, however, it is unnecessary to heat the carbonising apparatus; in fact, cooling it would be sounder practice. If no arrangements are provided for distributing the gas from a central point to the retort furnaces, and the gas evolved from each separate carbonising apparatus is conducted to its own furnace—a practice which is still quite common—it is impossible to avoid overheating the apparatus during the violent phase of carbonisation, thus causing rapid destruction of plant and reduction in yields.

During the process of condensation the non-condensable gases absorb components of pyroligneous acid to an extent corresponding to the temperature and pressure at which the gases leave the condensers—just as air becomes saturated with water vapour. The liquid products more especially affected are the low-boiling components of wood-naphtha, of which, in certain circumstances, very considerable amounts may be carried away by the gases. In one particular case the author found that no less than 5 per cent of the total production of acetic acid and wood-naphtha was passing off with the gas.

These valuable products must be recovered from the non-condensable gas by washing the latter with water. Interchange then takes place in the sense that the components of pyroligneous acid present in the gas are taken up by the washing water, and water vapour takes the place of those components in the gas.

Owing to the necessity of washing the gas and controlling its distribution for heating purposes, the only satisfactory method of operation is to unite the separate streams of gas issuing from the condensers into one main stream which can be dealt with as desired.

The hydraulic seal attached to each condenser is therefore connected with a gas-collecting main made of cast-iron, or better of copper, the latter being more durable and cheaper in practice. In large installations these collecting mains may attain very considerable dimensions.

With the object of rendering the necessity for cleaning the scrubber plant less frequent, another tar-separating apparatus, of the type used in the ordinary gasworks process, is placed between the wood-gas main and the scrubbers. This apparatus, by its beating action, extracts any entrained tar mist and eliminates it in the form of liquid.

The extraction of the components of pyroligneous acid from the wood-gas is carried out in scrubbers constructed of copper or possibly iron—in the latter case lined with brickwork—similar to those used in gasworks.

The use of scrubbers for washing the gas is not new, but the results obtained with them in the past were often unsatisfactory. The reason lay, not in the principle, but in the size, which was much too small.

However, by taking advantage of the experience obtained in the coal-gas industry, and by keeping the wood-gas for a sufficient length of time in contact with the finely divided washing water, the difficulties were successfully overcome. Small factories work with only one scrubber, larger factories employ two, which are connected either in parallel or in series—in the latter case with the object of enriching the washing water which is thus made to flow in counter-current to the stream of gas. Fig. 22 shows two scrubbers connected in parallel.

When the connection is in series, the path taken by the washing water is somewhat different. The gas then enters the

first scrubber near the bottom, flows upwards through the packing which consists of coke or preferably rolls of wood shavings, and escapes at the top through a pipe which conducts it into the lower portion of the second scrubber.

The washing water is supplied to Scrubber No. 2 by means of an automatic distributor connected with a water-tank. After passing down Scrubber No. 2 the water flows into a tank, from which it is supplied to Scrubber No. 1 by means of a pump, or monte-jus. The concentrated wash-water discharged from Scrubber No. 1 is returned to the process by running it into the collecting vat for crude pyroligneous acid, along with which it is subsequently worked up.

It may be reckoned that the washing water will amount to about 10-15 per cent of the weight of wood carbonised daily. Provided that a scrubber of the right dimensions is employed, the yield of acetic acid and especially of wood-naphtha will show a considerable increase.

On leaving the scrubbers, which at the same time play the part of gas-collecting apparatus, the gases enter the distributing main after passing first through another hydraulic seal; the latter prevents flames from striking back into the scrubber, in the possible event of an explosion occurring at the point where the gas is burnt, owing to the accidental presence of air in the gas.

Branch pipes, provided with stop valves, conduct the gas to the various points at which it is utilised—either for heating purposes, as in the furnaces of the carbonising plant, the boilers or the acetone plant, or for generating power in gas engines.

If the collecting and distributing pipes are of considerable length, or if resistance to the passage of the gas through the system is likely to be set up in any other way, it is usual to instal pressure fans between the carbonising apparatus and the scrubbers. A Roots blower or any other suitable form of blower, constructed in bronze, may be used for the purpose, but the operation of this apparatus must be carefully regulated, and a spare blower, which can be brought into operation immediately in the event of breakdown, must be provided.

No objection can be raised against the use of fans, as long as the resistances are only small and the retort is so constructed as to render it perfectly airtight.

Otherwise, air will enter the retort owing to the action of

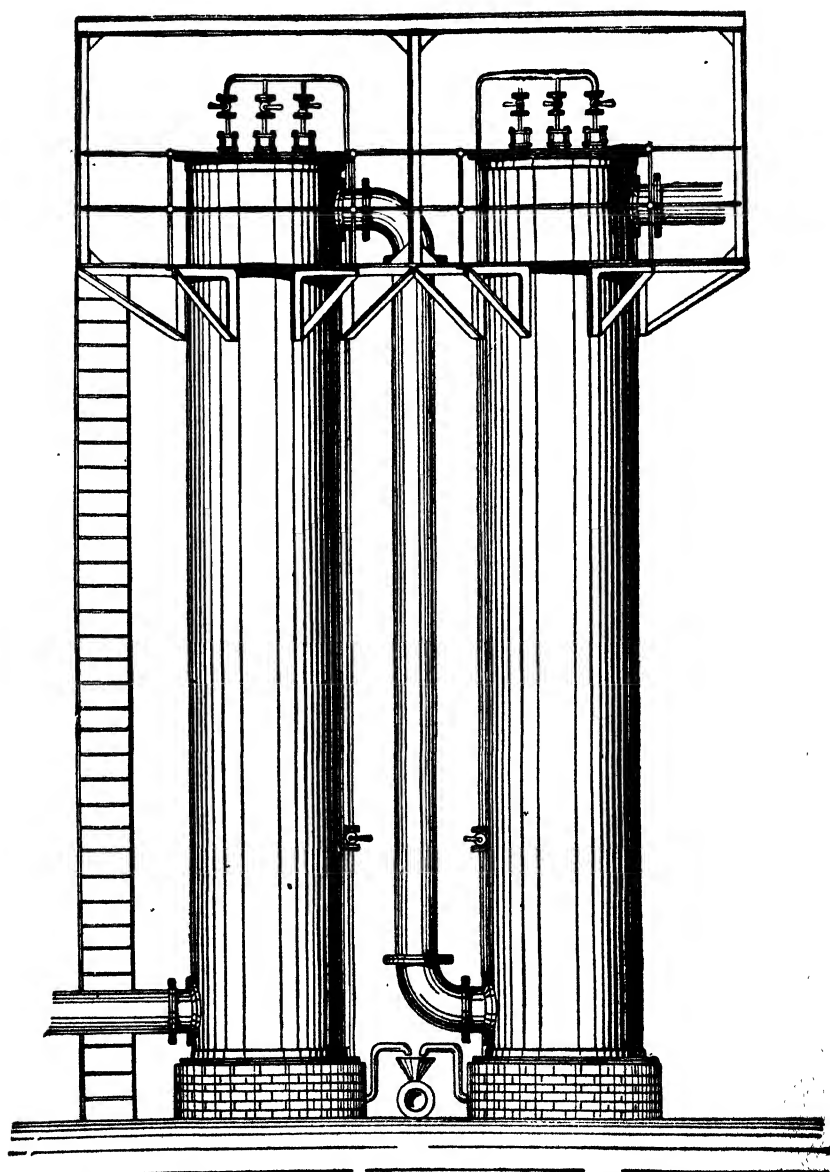


FIG 22.—PLANT FOR SCRUBBING THE NON-CONDENSABLE WOOD-GAS

the fan, and will cause a reduction in the yield of acetic acid and especially of wood-naphtha. This reduction is due in the first place to the combustion of a certain amount of acetic acid and oxidation of methyl alcohol to formaldehyde, and secondly, to the increase in the amount of non-condensable gas, with the result that the losses which arise from the absorption of components of pyroligneous acid by the gas are also increased. Moreover, if the suction is too strong and air is drawn into the carbonising apparatus, not only the quantity but also the quality of the products may be unfavourably affected, as the author observed during the operation of a patent rotary retort for the treatment of sawdust, etc. In this particular case a large proportion of the methyl alcohol was converted into formaldehyde, which could be clearly detected and quantitatively estimated in the pyroligneous acid.

On passing pyroligneous acid vapour containing formaldehyde through milk of lime, aldehyde-resins and compounds resembling formose are formed by the action of the free calcium hydroxide—and possibly the acetate of lime itself—on the aldehyde. These products remain mixed with the residue on evaporation (acetate of lime), with the result that the content of calcium acetate in the latter only reaches 65-71 per cent instead of 80 per cent. It is possible to dissolve out these conversion products of formaldehyde and to isolate them in considerable quantities by treating the acetate of lime with absolute alcohol; as a result the calcium acetate content of the product rises much above 80 per cent.

Provided that the retorts are perfectly airtight, the use of a fan for moving the gases is sound practice; large fans naturally consume a considerable amount of power, especially if the resistance in the suction and delivery pipes is at all high, and extra working costs are incurred accordingly.

The suitability of wood-gas for power purposes has already been discussed in detail on page 58.

CHAPTER XV

PRODUCTION OF CRUDE WOOD-NAPHTHA AND ACETATE OF LIME FROM CRUDE PYROLIGNEOUS ACID

I. ELIMINATION OF TAR FROM CRUDE PYROLIGNEOUS ACID

WHEN *hardwood* undergoes destructive distillation, the liquid product which is obtained chiefly from the condensers—but in certain circumstances partly beforehand—consists of a mixture of crude pyroligneous acid and tar. If the mixture is allowed to stand, the tar settles out as a separate layer below the acid, owing to its higher specific gravity. On the other hand, the condensed liquor derived from *softwood* contains terpenes and rosin-oils in addition to tar and acid. These products mingle with the tar and reduce its specific gravity, with the result that the terpene-tar mixture mostly floats on the surface of the acid.

The condensed liquor is conducted through a series of wooden vats, the capacity of which must correspond to a day's production. These vats are connected in series by means of overflow pipes, and the whole system, therefore, acts as a large Florentine receiver which separates the acid and the tar, or mixture of tar and terpenes, in accordance with their relative specific gravities, and delivers the products into separate collecting vats. From these vats the products are removed as required to undergo further treatment.

The normal components of crude pyroligneous acid from *hardwood* and *softwood* respectively have already been tabulated on p. 61. It has also been mentioned that crude pyroligneous acid is rarely saleable as such in any considerable quantity, and must therefore undergo further treatment for

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the purpose of obtaining marketable products in a form more suitable for export. Such products are :—

Brown acetate of lime, containing 67 per cent of calcium acetate.

Grey acetate of lime, containing 80 per cent of calcium acetate.

Crystallised sodium acetate.

Anhydrous sodium acetate.

“Iron liquor.”

Crude wood-naphtha.

Crude wood-naphtha is always obtained by distillation from the dilute solution of calcium or sodium acetate which is formed by neutralising pyroligneous acid with milk of lime or caustic soda solution. The methods employed for recovering this product are described elsewhere.

Crude pyroligneous acid always contains a certain amount of dissolved tarry matter which possesses quite characteristic properties.

The product known commercially as “*brown acetate of lime*” is obtained by neutralising the crude acid—containing dissolved tar—with milk of lime, distilling off the wood-naphtha, and evaporating the residual solution to a paste in directly heated or steam-jacketed pans. The tarry matter which separates out during the process is removed by skimming, and finally, the paste is dried on drying-floors which are heated by direct fire or furnace gases. The product is brownish- or greyish-black and, for the reasons stated on p. 64, its content of calcium acetate does not exceed 67 per cent. Formerly, this product represented practically the only form in which acetate of lime was manufactured and sold.

Brown acetate is quite unsuitable for the manufacture of acetone, or for the manufacture of acetic acid by decomposition with sulphuric acid, owing to the fact that it readily softens and becomes converted into a sticky mass. Less difficulty is experienced in decomposing brown acetate by hydrochloric acid, according to the older process of manufacturing acetic acid. This process was at one time in general use, but is now regarded as inefficient.

The acetic acid and acetone industries of to-day have no use for brown acetate of lime as a raw material, and modern wood-distillation factories are therefore more or less compelled

to manufacture a purer product, namely, "*grey acetate of lime*."

This object can only be achieved by eliminating the dissolved tar from the pyroligneous acid by some suitable process *before* neutralising the acid, since the presence of tar in the finished acetate of lime is the factor chiefly responsible for the objectionable behaviour of brown acetate of lime mentioned above.

The elimination of dissolved tar from crude pyroligneous acid is effected most easily by distillation. The tar (see p. 69) remains behind in the still, and the distillate consists of "*distilled pyroligneous acid*," which possesses the following approximate composition :—

	Distillate from crude beechwood pyroligneous acid. Per cent.	Distillate from crude softwood pyroligneous acid. Per cent.
Acetic acid	8.9	3.15
Wood-naphtha	3.2	1.56
Water	87.8	95.29
Residue on evaporation .	0.1	0.10

If acetic acid were the only organic acid present in distilled pyroligneous acid, exact neutralisation of 100 kilos. of the product from beechwood with milk of lime would give :—

$$60 : 79 = 8.9 : x$$

$$x = 11.71 \text{ kilos. of calcium acetate (100 per cent).}$$

In the first place, however, 0.1 kilo. of residual matter remains mixed with the acetate, and in addition the proportion of water of crystallisation which the salt is able to retain when dried at a temperature of 120° to 130° C. A higher temperature is inadmissible, since decomposition already sets in at 150° C. with formation of ketones and consequent loss of acetic acid.

Calcium acetate (mol. wt. = 158) when dried at 120°–130° C. retains one molecule of water. Hence 11.71 kilos. of calcium acetate (100 per cent) will retain :—

$$158 : 18 = 11.71 : x$$

$$x = 1.33 \text{ kilos. of water.}$$

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8.9 kilos. of acetic acid (=100 kilos. of distilled pyroligneous acid) will therefore furnish, theoretically :—

11.71 kilos. of calcium acetate (100 per cent).

1.33 „ water of crystallisation.

0.10 „ residue on evaporation.

13.14 kilos. of grey acetate of lime, dried at 125°.

A salt of this composition if analysed by the Fresenius method (p. 383) should show a content of :—

$$13.14 : 11.71 = 100 : x$$

$$x = 89.11 \text{ per cent calcium acetate.}$$

In practice, however, this content, though theoretically possible, is never reached if the pyroligneous acid has only undergone one distillation.

The maximum content of calcium acetate in the final product obtained from distilled beechwood acid is 82-84 per cent, and from softwood acid only 75-78 per cent.

The question now arises as to why the calculated values and those actually obtained in practice should exhibit such considerable differences. The reasons are to be found in the fact that neither the distilled pyroligneous acid nor the neutralising agent (lime) is a pure chemical compound. Besides acetic acid, the pyroligneous acid contains certain quantities of propionic and butyric acids. Since these homologues are estimated as acetic acid along with the latter, it follows that the presence of these foreign acids alone must bring about an apparent reduction in the strength of the acetate of lime. If the acids are present to the extent of 5 per cent, this reduction may amount to as much as 3-4 per cent. The presence of acids other than acetic, however, is not sufficient to account for the difference between the theoretically possible strength of acetate of lime and that obtainable in practice, especially in view of the fact that the strength of the product from softwood acid is essentially lower than that of the product from hardwood acid.

Another factor, exercising considerable influence on the concentration of the acetate of lime, must therefore be present.

We have seen that distilled acid liquor obtained from crude pyroligneous acid leaves only about 0.1 per cent of residue when evaporated at 100° C. This figure and the almost "water-

white" appearance of the acid liquor demonstrate that the latter no longer contains tarry components in the strict sense of the term.

On examining the acetate of lime produced by neutralising the acid with milk of lime, it is obvious that tarry matter is present in the product; moreover, by dissolving the acetate in hydrochloric acid it is possible to isolate the tarry matter.

Seeing that the initial product was free from tar, and that the final product contains tar, conditions must be set up in the process of neutralisation, or in the subsequent process of evaporation, which lead to the secondary formation of tar or products resembling tar.

It has already been mentioned that pyroligneous acid contains many substances of an aldehyde nature, together with phenols, quinones, etc.; in short, substances which readily undergo reaction with acids and more especially with alkalis, becoming converted into products such as aldehyde-resins, etc., which in appearance often completely resemble tarry matter.

The most sensitive of these substances are the aldehydes, which by heating with alkaline earths or even with salts of organic acids are readily converted into resinous or sugary masses.

Acetaldehyde and formaldehyde are always present in the liquid products of wood-distillation, and formaldehyde especially is not readily separable from the pyroligneous acid by any process of fractional distillation. If pyroligneous acid containing aldehydes is neutralised and the neutral solution is evaporated to dryness, the greater proportion of the aldehydes is converted into aldehyde-resin; in other words, volatile components of the acid combine with bases to form non-volatile substances which remain admixed with the residue on evaporation—the acetate of lime. In this way it is possible to account for the occurrence of tarry matter in commercial acetate of lime, though the distilled acid, before neutralisation, was completely free from tar. This explanation is supported by the fact that the "tarry matter" is soluble in water; it can be extracted from the acetate by means of alcohol, and the residue after evaporating off the alcohol exhibits the characteristic behaviour of aldehyde-resin.

It appears probable that the dissolved tar in the crude pyroligneous acid is of similar origin and arises by the action, while in a state of vapour, of certain constituents of pyroligneous

acid or tar on other products of the process of wood-distillation which readily undergo reaction. These reactions take place in the distillate from the carbonising apparatus during condensation, and the products of reaction are dissolved to a certain extent by the pyroligneous acid, or rather by the acetic acid and wood-naphtha present in that product.

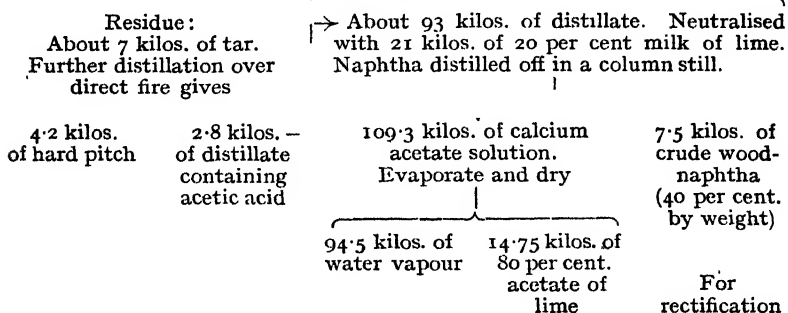
In order to convert crude pyroligneous acid into *grey acetate of lime* (80 per cent) it is essential, therefore, to distil the acid before neutralisation for the purpose of eliminating the "dissolved tar." Otherwise, the only possible product is *brown acetate of lime*, containing about 67 per cent of anhydrous calcium acetate.

At the present day *four* distinct processes are employed for converting pyroligneous acid into a solution of acetate of lime, from which, by subsequent evaporation and drying, a product containing at least 80 per cent of calcium acetate is obtainable. These processes are described below.

Process A.—Simple distillation of crude pyroligneous acid and subsequent neutralisation of the liquid distillate.

The simplest method of treating the acid would appear to be that shown in the following flow-sheet and employed almost exclusively in the American factories.

100 kilos. of crude pyroligneous acid (for composition see p. 63) are distilled, and produce:



This process is conducted in a copper still heated by means of high-pressure steam (Fig. 23). The pyroligneous acid undergoes simple distillation, as a result of which about 7 per cent of the original charge is left as a residue, consisting of

so-called dissolved tar (for composition see p. 69), and about 93 per cent is recovered as distillate.

Varying quantities of oils volatile in steam come over with the distillate, which, after condensation, constitutes the so-called "distilled pyroligneous acid." These oils partly float on the surface, and partly sink to the bottom, of the acid; they are removed mechanically by allowing the liquor to settle and then drawing off the oily layers, or else by allowing the liquor to flow continuously through a number of vats connected in series and acting as a Florentine receiver.

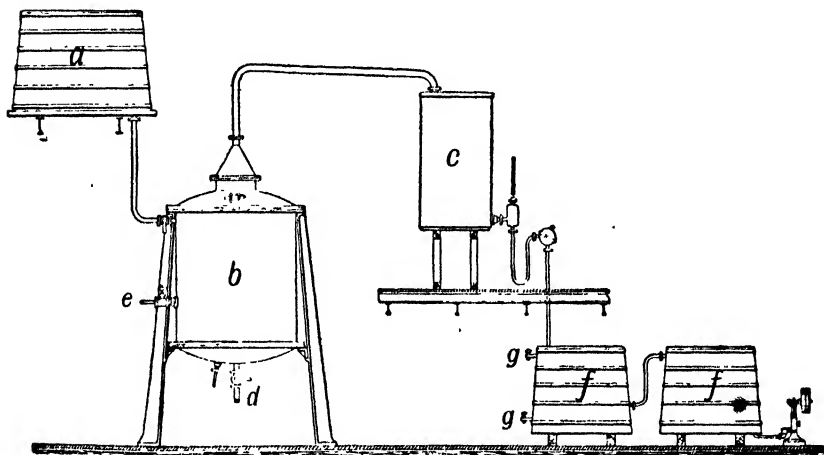


FIG. 23.—ARRANGEMENT OF PLANT FOR ELIMINATION OF TAR FROM CRUDE PYROLIGNEOUS ACID BY SIMPLE DISTILLATION

a, crude pyroligneous acid vat; *b*, copper still; *c*, condenser; *d*, outlet for tar; *e*, steam inlet; *f*, collecting vat for distilled acid; *g*, oils run-off cocks.

After the oils have been removed, the distilled acid, which contains as its more important components acetic acid and wood-naphtha—the latter a mixture consisting chiefly of methyl alcohol, methyl acetate, acetone and allyl alcohol—is treated for the removal of naphtha. This operation is carried out either by distilling off the naphtha directly from the acid liquor, or preferably, by treating the liquor with milk of lime until it is slightly alkaline, and then removing the naphtha by distillation. The former method produces wood-naphtha containing not only free acetic acid, but also a relatively large proportion of methyl acetate; in this way,

appreciable loss of acetic acid may arise. Removal of naphtha directly from the acid liquor is therefore inadvisable. The second method—namely, removal of the naphtha after the process of neutralisation—furnishes a product which is free from acid and contains only a small amount of methyl acetate. The second method is therefore almost invariably adopted.

Neutralisation of distilled pyroligneous acid. The process of neutralisation is carried out in closed wooden vats fitted with stirring apparatus. During the process, precipitates are formed, partly by the action of impurities present in the milk of lime (for example, basic aluminium acetate, basic ferric acetate), and partly by the action of milk of lime on certain constituents of pyroligneous acid—such as acetaldehyde, formaldehyde, pyrocatechol, phenols, etc.—resulting in the formation of organic calcium compounds which may give rise to certain difficulties owing to their viscid and sticky nature.

This deposit or sludge is usually eliminated by settling the liquor, or possibly by filtration through a filter press; after separation the sludge is washed. The ease with which the filtration can be carried out depends on the degree of neutralisation. If the liquor remains acid, filtration is relatively difficult, whereas liquor exhibiting a distinctly alkaline reaction can be filtered with comparative ease. The filtered acetate solution, which, if derived from beechwood pyroligneous acid, will contain about 10 per cent of calcium acetate, is then treated by a continuous or intermittent process of distillation for the removal of wood-naphtha. The resulting distillate contains from 40 to 95 per cent of wood-spirit, according to the type of apparatus employed; and the residual liquor consists of a solution of calcium acetate, free from naphtha, which is worked up into solid acetate of lime by processes of evaporation and drying.

The methods employed for isolating wood-naphtha and recovering acetate of lime will be described later.

A sound basis on which to compare the values of the different methods of eliminating tar from pyroligneous acid by distillation is the amount of fuel consumed, since the latter represents the chief cost of working up the acid.

It will be necessary, therefore, to calculate the relative amounts of fuel required for carrying out the different processes.

Assuming the following values for the latent heats of vaporisation :—

85 kilo-calories per 1 kilo. of acetic acid at 118° C. and 760 mm. pressure

264 kilo-calories per 1 kilo. of methyl alcohol at 66° C. and 760 mm. pressure

536 kilo-calories per 1 kilo. of water at 100° C. and 760 mm pressure

and neglecting the slight deviations from these values, due to the differences in the state of saturation of acetic acid and methyl alcohol vapour at the temperature of vaporisation of the pyroligneous acid (100° C.), the mean latent heat of vaporisation of crude beechwood pyroligneous acid at 100° C. works out as follows :—

$$\begin{array}{rcl}
 8.9 \times 85 & = & 756.5 \\
 3.2 \times 264 & = & 844.8 \\
 87.8 \times 536 & = & 47,060.8 \\
 \hline
 99.9 \text{ kilos.} & = & 48,662.1 \text{ kilo-calories} \\
 \frac{48,662.1}{99.9} & = & 487 \text{ kilo-calories per 1 kilo.}
 \end{array}$$

Hence, the process of working-up the pyroligneous acid, as set out in the flow-sheet on p. 200, requires the following expenditure of heat :—

	Kilo-calories.
(a) 100 kilos. of pyroligneous acid heated from 20° to 100° (assuming sp. ht. = 1):	
	$100 \times (100 - 20) = 8,000$
(b) 93 kilos. of pyroligneous acid distilled off:	
	$93 \times 487 = 45,291$
(c) 116.8 kilos. of calcium acetate solution heated to 100° and naphtha distilled off ¹ :	$= 7,888$
(d) 94.5 kilos. of water evaporated from 109.3 kilos. of acetate solution:	$94.5 \times 536 = 50,652$

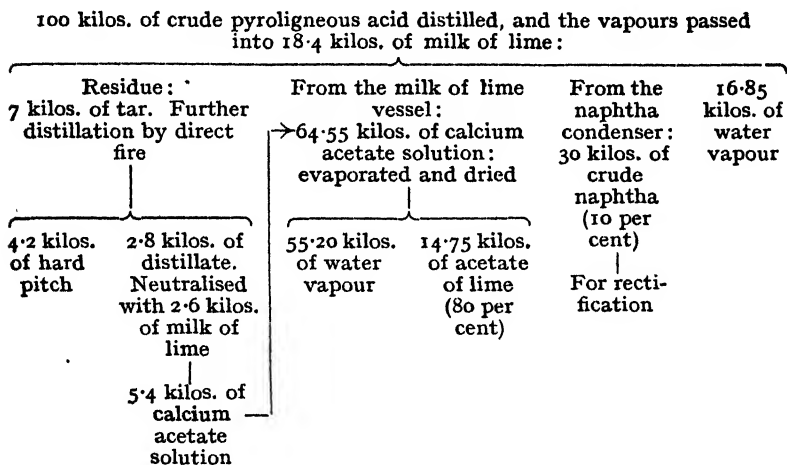
Total amount of heat required theoretically for the above operations, according to Process A:

111,831.

¹ See Hausbrand, "Wirkungsweise des Rektifizierapparates," 1893, p. 83.

Process B.—Distillation of pyroligneous acid and simultaneous neutralisation of the acid vapour by means of the so-called three-vessel system.

The methods of procedure, as well as the amount of fuel consumed, differ completely if the mixture of water vapour, acetic acid and wood-naphtha resulting from the distillation of crude pyroligneous acid is passed directly into milk of lime without previous condensation, and the apparatus is so arranged that the vessels which contain the milk of lime, and which are connected with the acid still and a condenser, can be brought into, or thrown out of, action without interruption of the process. In these conditions the process assumes the form shown in the following flow-sheet :—



In its simplest form the apparatus employed for carrying out these operations consists of a combination of three vessels provided with a condenser. The largest of these vessels is always constructed of copper and is fitted with a copper steam coil ; it is charged with crude pyroligneous acid, usually from a vat placed at a higher level, and the charge is then heated to boiling by means of the steam coil. The other two vessels, which may be constructed of iron, are charged previously up to about 30 per cent of their capacity with milk of lime (20 per cent).

A perforated delivery pipe passes from the first vessel to the bottom of the second vessel, and a similar pipe connects

the latter with the third vessel, which usually stands at a higher level. Finally, the third vessel is connected by a delivery pipe with the condenser.

Each vessel is provided with special safety valves, which prevent the occurrence of a vacuum and, as a consequence the possible collapse of the copper vessel or the suction of liquor from one vessel to another.

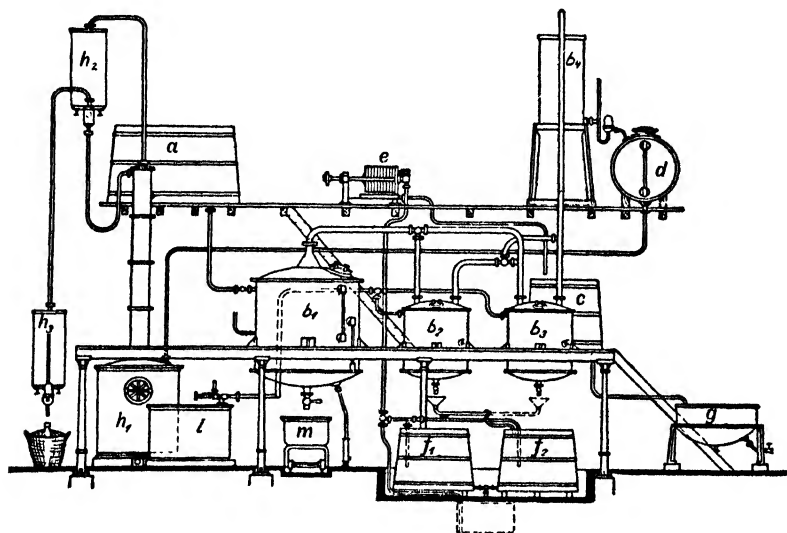


FIG. 24—THREE-VESSEL SYSTEM.

a, pyroligneous acid vat; *b*₁, acid still; *b*₂ and *b*₃, milk of lime vessels; *b*₄, condenser for naphtha vapour from *b*₂ and *b*₃; *c*, settled acetate liquor vat; *d*, collecting tank for dilute naphtha; *e*, filter press; *f*₁, *f*₂, collecting vats for acetate liquor from *b*₂ and *b*₃; *g*, evaporating pan; *h*₁, pot-still for rectification of dilute naphtha; *h*₂, dephlegmator; *h*₃, condenser; *l*, lime-mixer; *m*, tar tank.

The vapours evolved from the first vessel—consisting of water, acetic acid and its homologues, together with the components of wood-naphtha—pass into the milk of lime contained in the second vessel, and are condensed there until the contents of the vessel have reached the boiling point.

The vapours escaping from the second vessel—mainly water and the components of naphtha—still contain small traces of acetic acid which have escaped absorption owing to the rapid rate of flow of the vapour through the milk of lime.

The process in the third vessel is similar to that in the second, but the vapours escaping from the third vessel consist only of water and wood-naphtha. Since the latter is the most volatile component of pyroligneous acid, it naturally passes over first into the condenser, from which it is obtained as aqueous naphtha with a concentration of 30-40 per cent.

Since the dimensions of the second and third vessels usually do not permit the whole quantity of milk of lime to be used in one charge, it is necessary to make occasional tests in order to determine to what extent the milk of lime in the second vessel has been neutralised. An expert operator is able to recognise the point of complete neutralisation solely from the appearance of a sample, or even from its odour; the degree of neutralisation may also be determined by testing samples of the liquor with suitable reagents.

The naphtha, which comes over in the beginning at a concentration of about 30-40 per cent, gradually becomes weaker. After a volume equivalent to about 30 per cent of the original charge of pyroligneous acid has been obtained from the condenser, it is no longer possible to detect the presence of naphtha in the distillate by means of the alcoholometer—an indication that the naphtha period is completed.

The average concentration of naphtha in the distillate is about 10 per cent.

As soon as the naphtha period is over, the condenser is thrown out of action, and the vapours from the third vessel are allowed to escape through an open manhole; or they may be conducted away by means of special piping and utilised elsewhere for the purpose of preheating.

While the vapours evolved from the crude pyroligneous acid are passing through the milk of lime, numerous chemical reactions take place. Primarily, the acetic acid and its homologues react with the lime to form calcium acetate, etc.; methyl acetate becomes hydrolysed with the formation of calcium acetate and methyl alcohol.

Apart from these reactions, for which of course the process provides, secondary reactions also take place, especially the conversion of aldehydes (formaldehyde, acetaldehyde, furfural) into more or less resinous products. The latter partly separate out and partly remain in solution, thus giving rise to the so-called "tar content" of the final product. A portion of the light tar-oils and phenols is also partly hydrolysed by the milk

of lime and partly emulsified and retained. The final product resulting from the process of neutralisation consists of a coffee-coloured turbid liquid possessing a peculiar pungent odour. If neutralisation has been carried to the right point, the liquid gradually clarifies and at the same time deposits a coffee-coloured sludge which consists of the insoluble impurities present in quicklime (sand, etc.), together with basic acetates of iron and aluminium, and compounds of lime with resinous conversion products of aldehydes and phenols.

If neutralisation has been carried to the right degree—that is, to leave the liquor slightly alkaline—the elimination of suspended matter, either by settling or by filtration through a filter press, offers no difficulties.

When the contents of the second vessel have reached this condition, the process must be interrupted in order to permit discharge of the vessel. In the first place the air-valves of vessels I and II are opened and the supply of steam to vessel I is cut off. After a few minutes the evolution of vapour ceases, and the contents of vessel II may be discharged into the corresponding collecting tank. The milk of lime from vessel III is then run into vessel II, vessel III is charged with fresh milk of lime, the supply of steam to vessel I is turned on again, and the process continues as before.

Distillation is carried on until evolution of vapour ceases. The residue then remaining in the first vessel consists of more or less concentrated tar containing a considerable quantity of acetic acid (see analysis, p. 69). It is usual to work off a number of charges in the vessel before removing the tar. When a sufficient quantity has accumulated, it is discharged and subsequently freed from acetic acid.

A great advantage of the three-vessel process is that, simultaneously with the elimination of tar from crude pyroligneous acid, the wood-naphtha is removed from the acetate solution and the latter is concentrated by the stream of vapour passing through the liquor.

This process results in the production of a solution containing 20–25 per cent of calcium acetate, and a distillate containing about 10 per cent of wood-naphtha.

On the whole this process works very satisfactorily, but a considerable number of modifications have been suggested.

One great disadvantage attaching to the method described

above is the necessity of stopping the distillation every time it is required to discharge the acetate liquor.

Fig. 25 shows the details of a modification by means of which the distillation can be carried on without interruption while the acetate liquor is being discharged.

This is rendered possible by fitting the delivery pipe from the first vessel with a three-way cock. The pipe can then be brought into connection either with the second vessel or with the third; thus, each vessel can be made to act either as second or third. By means of a similar arrangement the vapour pipes from these vessels can be brought into connection with the delivery pipe to the condenser.

When the contents of the second vessel are neutralised, that vessel is thrown out of action, emptied and re-charged with milk of lime. During this short period the vapours pass from vessel I into vessel III alone. As soon as vessel II is ready it is brought into action again; the direction of the flow of vapour is into vessel III in the first place, thence into vessel II, and finally into the condenser.

An arrangement of this kind renders it possible to work off a charge of crude pyroligneous acid without interruption; but it does not permit completely continuous operation—that is, the distillation of pyroligneous acid which is being supplied in a continuous stream to the apparatus.

Continuous three-vessel system. This plant also consists of three interconnected vessels. Preheated pyroligneous acid flows continuously into the first vessel, which is connected with the vessels containing milk of lime on the by-pass system described above. These vessels can therefore be charged and discharged without interrupting the distillation.

The continuous process differs from the intermittent process in regard to the concentration of the naphtha produced. The latter process furnishes a solution containing, on an average, 10 per cent of naphtha, owing to the fact that in distilling a given charge of acid the naphtha tends to concentrate in the first portion of the distillate. If, however, the pyroligneous acid is distilled continuously, concentration of naphtha in the above manner does not take place; the limit of concentration which the product can attain is governed by the amounts of tar and calcium acetate solution passing out of the process.

According to the flow-sheet on p. 204, 100 kilos. of pyroligneous

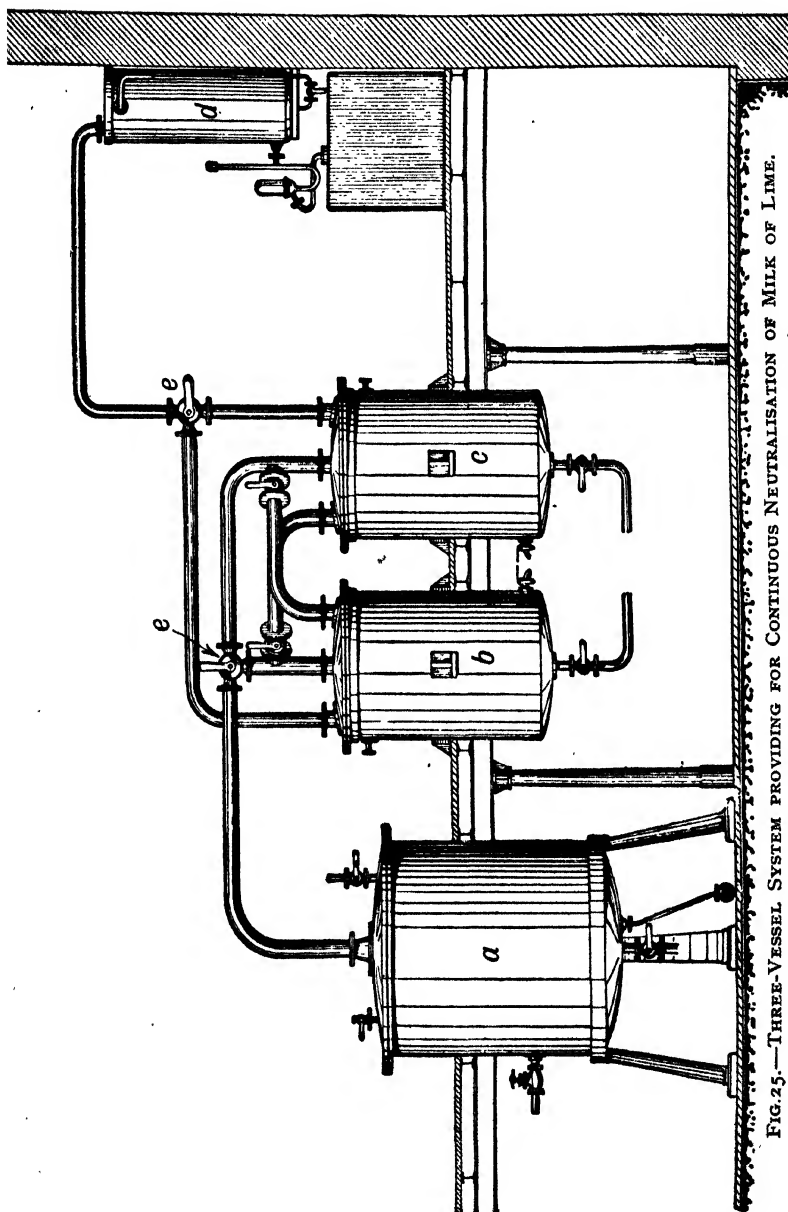


FIG. 25.—THREE-VESSEL SYSTEM PROVIDING FOR CONTINUOUS NEUTRALISATION OF MILK OF LIME.

a, crude pyroligneous acid still ; *b*, *c*, milk of lime vessels ; *d*, condenser for naphtha vapours from *b* and *c* ; *e*, *e*, three-way cocks.

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acid and 18.4 kilos. of milk of lime (total = 118.4 kilos.) produce 71.55 kilos. of tar + calcium acetate solution. The difference between these totals corresponds to the weight of crude naphtha condensed, namely :—

$$118.4 - 71.55 = 46.85 \text{ kilos.},$$

and the strength of the product is only about 6.4 per cent as against 10 per cent for the product from the intermittent process.

Experience has shown¹ that the amount of steam required for the rectification of solutions containing between 10 and 50 per cent of naphtha is practically constant, whereas solutions containing under 10 per cent require a considerably greater quantity of steam to produce distillates of similar quality.

For this reason it is now customary, when the continuous three-vessel process is adopted, to instal dephlegmators between the third vessel and the condenser. By this means water vapour is condensed out of the mixture of water vapour and wood-naphtha vapour in sufficient quantity to render the naphtha concentration of the distillate higher than 10 per cent.

Concentration of the distillate to a still higher degree results in very little economy in steam consumption; on the other hand, a smaller pot-still can then be used for the preliminary rectification of the naphtha distillate, assuming that the modern continuous system of distillation is not adopted.

The use of dephlegmators between the last vessel and the condenser has also been recommended for the intermittent three-vessel plant, but this additional complication is only justifiable if the naphtha distillate comes over at an average concentration of less than 10 per cent—as, for example, from softwood pyroligneous acid.

The following table indicates the amount of heat required to work up 100 kilos. of pyroligneous acid from air-dry beech by the normal intermittent three-vessel process :—

	Kilo-calories.
(a) 100 kilos. of pyroligneous acid heated from 20° C. to 100° C. (assuming sp. ht. = 1) :	
	$100 \times (100 - 20) = 8,000$
(b) 93 kilos. of pyroligneous acid distilled :	
	$93 \times 487 = 45,291$
(c) 55 kilos. of water evaporated from 70 kilos. of acetate solution :	
	$55 \times 536 = 29,480$
	Total = <u>82,771</u>

¹ Hausbrand, *loc. cit.*

Hence, 100 kilos. of pyroligneous acid, when treated by Process B, require theoretically an expenditure of 82,771 kilo-calories as against 111,831 kilo-calories for Process A.

Although these figures are deduced theoretically, they are none the less valid for purposes of comparison. They demonstrate that Process B, compared with Process A, results in a saving of about 25 per cent in expenditure of heat.

Process C.—Treatment of crude pyroligneous acid by the reduced pressure process of F. H. Meyer.¹

Process A is open to certain modifications which considerably reduce the consumption of steam and form the basis of the above-mentioned patent process.

As shown in the Patent Specification, this process depends on repeated utilisation of the latent heat which is present in the water vapour produced on evaporating the solution of calcium acetate, and also in the vapour mixture evolved during the distillation of crude pyroligneous acid or of the wood itself.

The temperature of the water vapour formed by the evaporation of calcium acetate solution is approximately the same as the temperature of boiling pyroligneous acid; at atmospheric pressure, therefore, it is impossible to utilise either the water vapour or the pyroligneous acid vapour to effect further distillation or evaporation, since the difference in temperature between the heating agent and the liquor to be distilled is not sufficiently great.

Repeated utilisation of the latent heat can be rendered practicable, however, by evaporating the acetate solution under increased pressure and employing the high-pressure vapour evolved to distil the pyroligneous acid; or else by evaporating the acetate solution under atmospheric or slightly reduced pressure, and using the vapour evolved to distil pyroligneous acid which is kept under reduced pressure during distillation. The process can, of course, be inverted.

The first method—namely, evaporation of acetate solution under pressure—involves the use of high-pressure steam. By adopting the second method, however, which consists in maintaining a vacuum, increasing by stages, in the evaporating plant or in the acid distillation plant, use can be made of any suitable source of waste heat, such as exhaust steam from

¹ German patent 193,382 (owned by F. H. Meyer, Hannover-Hainholz; introduced by the author of this book).

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engines or pumps, furnace gases, the mixture of gas and vapour evolved from the retorts, etc.

Since waste steam or waste gases are always available in a wood-distillation factory, the second method—namely, evaporation under reduced pressure according to the patent process mentioned above—is of greater interest from the practical point of view.

In the flow-sheet on p. 200 it was shown that 100 kilos. of crude pyroligneous acid from beechwood produce 109.3 kilos. of acetate solution at a concentration of 13.49 per cent. On evaporation, solutions of calcium acetate begin to deposit the crystalline salt when a concentration of 33–35 per cent is reached. *Hence, in closed evaporators it is impracticable to attain a higher concentration than 33 per cent.*

109.3 kilos. of acetate solution at 13.5 per cent are equivalent to 45 kilos. of solution at 33 per cent; hence, in order to reach the latter concentration it is necessary to evaporate $109.3 - 45 = 64.3$ kilos. of water.

The flow-sheet referred to above also shows that 93 kilos. of acid liquor must be distilled from the crude pyroligneous acid. The amount of heat available in 64.3 kilos. of water vapour evolved from the acetate solution $= 64.3 \times 536 = 34,464$ kilo-calories. On the other hand, the amount of heat required to produce 93 kilos. of distilled acid $= 93 \times 487 = 45,291$ kilo-calories.

Hence, in these conditions it is impossible to distil the acid by means of the water vapour resulting from the evaporation of the acetate solution, even if the necessary difference in temperature, which must exist between the heating medium and the liquid to be distilled, is attained by carrying out the process in a vacuum.

If, however, the liquors to be evaporated and distilled are divided into three portions, and the process is so conducted that the 64.3 kilos. of water vapour from the acetate solution are utilised to vaporise 50 kilos. of acid, and the latent heat of the latter ($= 50 \times 487 = 24,350$ kilo-calories under atmospheric pressure) is again utilised to vaporise the remainder of the acid ($93 - 50 = 43$ kilos.), it is then possible to distil the acid by means of the latent heat contained in the water vapour resulting from the evaporation of the acetate solution. If waste steam or waste gases are available, the distillation is free of cost. Even if no waste sources of heat are available, only a fraction of the steam required by the ordinary distillation process is necessary.

This process is particularly suitable for large factories, several of which have adopted it. The apparatus consists of a multiple

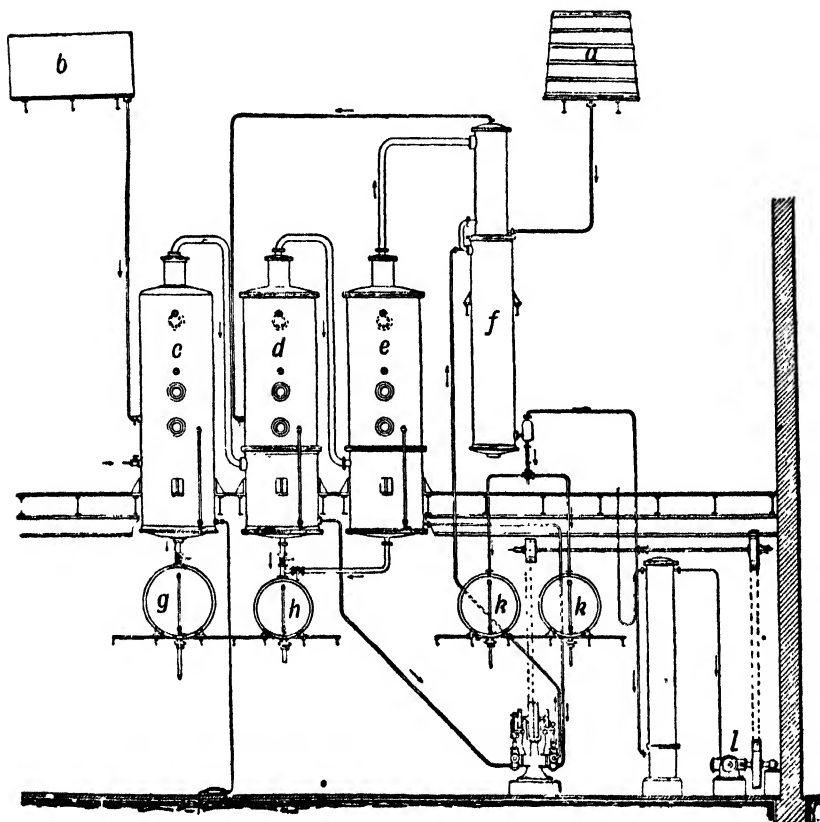


FIG. 26.—APPARATUS FOR THE CONTINUOUS DISTILLATION OF PYROLIGNEOUS ACID BY MEANS OF EXHAUST STEAM OR OTHER SOURCES OF WASTE HEAT,¹ WITH SIMULTANEOUS EVAPORATION OF CALCIUM ACETATE SOLUTION.

a, pyroligneous acid vat ; *b*, acetate liquor tank ; *c*, first vessel ; *d*, second vessel ; *e*, third vessel ; *f*, condenser ; *g*, receiver for concentrated acetate liquor ; *h*, receiver for tar ; *k, k*, interchangeable receivers for distilled acid ; *l*, vacuum pump.

evaporator connected with a vacuum pump which maintains a graduated vacuum in the apparatus. Fig. 26 shows the disposition of an apparatus of this type.

¹ German patent 193,382.

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If a triple-effect is employed the first vessel will contain the acetate solution, which, under a pressure of 550 mm. (mercury), boils at 90°C . and can therefore be evaporated by means of waste steam or waste gases (temperature=about 103°C .). The water vapour at 90°C . passes into the heating system of the second vessel which contains pyroligneous acid. In the second vessel a pressure of about 200 mm. is maintained. Under this pressure the acid boils at $70\text{--}80^{\circ}\text{C}$., hence water vapour at 90°C . is able to effect the distillation of the acid. The acid vapours leave the second vessel at a temperature of $70\text{--}80^{\circ}\text{C}$. and pass into the heating system of the third vessel which also contains pyroligneous acid. The pressure in the third vessel is 160 mm., and the acid boils at 60°C .; the vapours from the second vessel are therefore at a sufficiently high temperature to distil the acid in the third vessel. These vapours, on entering the heating system of the third vessel, give up their latent heat and condense to a liquid possessing the same temperature as the vapours leaving the third vessel (60°C .).

The third vessel is connected with a condenser in which the vapours passing over from that vessel are condensed and cooled. The condenser discharges into interchangeable receivers which are connected with the air-pump.

Thus one half of the distillate is furnished by the heating system of the third vessel, and the other half by the condenser.

Both the calcium acetate solution and the crude pyroligneous acid are fed continuously into the plant; thus the whole process, which includes concentration of the former and distillation of the latter, is carried out in a single continuously-operating apparatus which also provides for the preheating of the crude acid free of cost.

The amount of heat required, theoretically, by the process works out as follows :—

	Kilo-calories.
(a) 100 kilos. of pyroligneous acid (preheated to 50°C . by the vapours from the third vessel) heated from 50° to 70°C . :	
$100 \times (70 - 50) =$	2,000
(b) 116.8 kilos. of acetate solution heated to 100° and the naphtha distilled off (see p. 203) : =	7,888

(c) 94.5 kilos. of water vapour evaporated from 109.3 kilos. of calcium acetate solution :	
	$94.5 \times 536 =$ 50,652
(d) Heat expended in generating power for driving the pump :	2,500
Total =	<u>63,040</u>

A large proportion of the heat required—especially the 2,000 kilo-calories included under (a), and about 30,000 kilo-calories out of the amount included under (c)—can be furnished by the exhaust steam from an engine, or by some other source of waste heat (waste gases, etc.). In this case the process requires only about 31,000 kilo-calories for the treatment of 100 kilos. of crude pyroligneous acid, whereas—in the same conditions—the old system of distillation in one vessel (Process A) requires 111,831 kilo-calories and the three-vessel system 82,771 kilo-calories.

These figures demonstrate that great economy in fuel-consumption is effected by employing the patent process described above. In addition, there is also a considerable saving in capital cost and charges for labour.

It has already been mentioned that, in addition to the exhaust steam from engines and pumps; other sources of waste heat available in a wood-distillation factory may be employed for the purpose of distilling pyroligneous acid or evaporating acetate liquor.

The only process which can be considered in connection with the use of such sources of waste heat is the simple distillation of crude pyroligneous acid and subsequent neutralisation of the distilled liquor, as described for Process A. On p. 203 it was shown that the amount of heat required (1) for the distillation of 100 kilos. of crude pyroligneous acid = 53,291 kilo-calories, and (2) for the total evaporation of the water from the resulting calcium acetate solution = 50,652 kilo-calories. It must be noted, however, that the latter figure refers to the amount of water which must be evaporated in order to obtain acetate of lime in a completely dry state. In actual practice final drying is always carried out in special drying plant, and the acetate when introduced into the plant contains 50 per cent of water.

In consequence the theoretical amount of heat required for

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the concentration of the acetate liquor—from 100 kilos. of crude acid—is reduced to $79.7 \times 536 = 42,719$ kilo-calories, as against 53,291 kilo-calories required for the distillation of pyroligneous acid.

Assuming that 100 kilos. of crude acid are obtained from 200 kilos. of hardwood ($=\frac{1}{2}$ cu. metre), then the following amounts of heat are required per 1 cu. metre of hardwood :—

	Kilo-calories.
Distillation of pyroligneous acid	106,582
Evaporation of acetate liquor to the consistency of a paste	85,438

From these figures it will be seen that every effort should be directed towards devising a method for the distillation of pyroligneous acid free of cost, especially in view of the fact that evaporation of acetate liquor offers greater difficulties owing to its tendency to form deposits on the heating surfaces.

The most advantageous method of utilising exhaust steam in this connection has been described above, and we will now consider the possibility of utilising other sources of waste heat.

Every wood-distillation factory contains the following sources of heat, of which, as a rule, no use is made :—

1. Waste flue gases from the retorts and boilers.
2. The volatile products of distillation which issue from the retorts and are deprived of their latent heat and superheat in the condensers.

According to the nature of the distillation process, between 60 and 100 kilos. of coal (at 7000 kilo-calories), or an equivalent quantity of any other suitable form of fuel, are required for carbonising 1 cu. metre (400 kilos.) of wood and working up the distillate to acetate of lime and wood-naphtha. Assuming that the maximum requirement is 100 kilos., and reckoning the amount of air supplied in practice as double the amount theoretically required for the combustion of the coal, then about 20 kilos. of furnace gases are obtained per 1 kilo. of coal burnt; or $100 \times 20 = 2000$ kilos. of furnace gases per 1 cu. metre of wood (400 kilos.) carbonised. It will also be assumed that these gases can be utilised for the above-mentioned purposes at a temperature of 300° C.

In order to avoid the necessity of using artificial draught

the gases must not be cooled below 230° C. before entering the chimney. Assuming that the specific heat of the gases $= 0.25$, the amount of heat which is rendered available in this way does not exceed $2000 \times (300 - 230) \times 0.25 = 35,000$ kilo-calories per 1 cu. metre of wood carbonised, whereas, theoretically, 106,582 kilo-calories are required for the distillation of the acid alone, and 85,438 kilo-calories for the evaporation of the acetate liquor.

The amount of heat available in the furnace gases is less than 20 per cent of the total requirement, and is therefore much too small to render practical utilisation worth considering.

It is obviously useless to complicate the process in the slightest degree for the sake of utilising this amount of heat; if the gases were used in this manner, complication would be unavoidable owing to the necessity of providing considerably greater heating surfaces.

We may now consider the possibility of utilising the heat available in the *volatile products of the carbonisation process*. On p. 104 this was shown to amount to a total of 147,440 kilo-calories per cu. metre of wood, made up as follows:—

122,000 kilo-calories, representing the latent heat contained in 200 kilos. of pyroligneous acid + tar (calculated as water).

25,440 kilo-calories, representing the amount of superheat contained in 200 kilos. of pyroligneous acid + tar (calculated as water) and 100 kilos. of wood-gas.

Owing to the presence, in solution, of tar and calcium acetate respectively, both the acid and the acetate liquor boil above 100° C.; hence, it follows that the heating agent must leave the heating system at a temperature above 100° , and therefore in the form of vapour. Assuming that the distillation of the acid and the evaporation of acetate liquor are carried out under atmospheric pressure in vessels provided with heating systems through which the volatile products from the carbonising apparatus are passed, it is obviously impossible to utilise the latent heat contained in the vapour of pyroligneous acid.

In the above conditions it is only possible to utilise the superheat, which amounts to 25,440 kilo-calories out of a total of 147,440 kilo-calories present in the gases, or about 13.5 per cent of the amount of heat required theoretically for the

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distillation of the acid and the evaporation of the acetate liquor.

This quantity of heat (25,440 kilo-calories) would at the most only suffice to preheat the acetate liquor and to a certain degree the pyroligneous acid; for this purpose, however, more convenient sources of heat are available.

The conditions are more favourable if the above processes are carried out under reduced pressure, in accordance with the principles described above.¹

By this method it is possible to bring the boiling points of both liquids below 100° C., and also to ensure that the heating agent shall leave the apparatus at a temperature below 100° C. and therefore in the form of liquid. Moreover, it is possible to utilise not only the superheat of the volatile products of carbonisation, but also the latent heat which amounts to about 122,000 kilo-calories.

Since, theoretically, only 106,582 kilo-calories are required (see above) for the distillation of the pyroligneous acid from 1 cu. metre of wood, it is obvious that in these conditions the heat available in the vapours from the carbonising apparatus is quite sufficient to distil the whole of the crude pyroligneous acid.

The process is carried out most suitably by uniting the products from several retorts and thus obtaining a more or less regular stream of vapour and gas, which is passed into the heating system of a copper vacuum apparatus.

The hot liquid product which results from the condensation of the vapours is passed, together with the non-condensable gases, through a second condenser; this is cooled with water, and plays the same part as the condensers ordinarily connected with the retorts—that is, it delivers crude pyroligneous acid and tar as a cold liquid mixture, and cools the non-condensable gas.

The boiling pan of the vacuum apparatus is connected with a condenser which delivers into two interchangeable receivers connected with the vacuum pump.

In operating vacuum apparatus it is essential that the heating agent be introduced at a very regular rate, if frothing over is to be avoided. This condition is not fulfilled, however, by the volatile products from the retort; the rate of flow is by no means uniform, and though the irregularity is reduced

¹ German patent 193,382

to some extent by combining several retorts and conducting the volatile products to a central main, it is not entirely eliminated.

Moreover, the total heat effect is no better than that obtained by the use of waste steam, which is almost always available in sufficient quantity; the apparatus is much more complicated, and finally, the process described in the next section gives equally good results, which can always be obtained with absolute certainty, by the use of a very simple apparatus operating at ordinary pressures. In view of these facts it is obvious that the form of vacuum process in which the vapours from the retort are used as the heating agent cannot be recommended.

Process D.—Treatment of pyroligneous acid by the tar-separator process of F. H. Meyer.¹

In all the processes dealt with so far, elimination of tar is effected by distilling the crude pyroligneous acid before neutralisation with milk of lime. Process D, on the other hand, is based on the separation of tar in liquid form directly from the gaseous mixture issuing from the carbonising apparatus, previous to the condensation of the pyroligneous acid.

The mixture of vapour and gas produced by the destructive distillation of wood leaves the carbonising apparatus at a temperature of 250–350° C., and possesses the following composition :—

	Per cent by weight.
Water vapour (b.p. 100° C.)	52.0
Acetic acid vapour (b.p. 118° C.)	6.7
Wood-naphtha vapour (b.p. 66° C.)	2.0
Tar mist or vapour	6.7
Gas	32.6

Water vapour, acetic acid vapour, naphtha vapour and the non-condensable gas leave the retort in an unsaturated and therefore superheated state; hence, these products are capable of parting with a certain amount of heat, without any danger of passing at the same time into the liquid state. The tar vapour, on the other hand, behaves quite differently.

Assuming that the high-boiling tarry products leave the

¹ German patent 189,303 (introduced by the author).

apparatus in the form of tar mist at an average temperature of 250–300° C., it follows that the mixture of gas and vapour must be saturated in respect of the components of tar, since the boiling points of these components lie mostly above that temperature.

If the mixture be gradually cooled to 100° C., its saturation capacity for tar will be correspondingly reduced, and a large proportion of the tar will separate out in the form of liquid. At that temperature (100°), however, very little pyroligneous acid vapour will condense.

If this process of gradually cooling the mixture be carried out in a series of separate vessels or cells, the temperature in any particular vessel will depend on the position of the latter in relation to the first vessel.

In each separate vessel a certain amount of heat will be lost by radiation, and a certain amount will be transformed into work as the stream of vapour and gas passes through the condensed liquid.

As a result of the loss of heat in each vessel, a certain amount of vapour becomes condensed to liquid, which in the first vessel—in view of the higher temperature—will consist chiefly of tar; in the last vessels, on the other hand, where the temperature is only 100° C., the condensed liquid will consist chiefly of pyroligneous acid together with only a small amount of tar.

In course of time, a liquid of definite composition, through which the vapours and gases are forced to pass, collects automatically in each cell.

If the apparatus is so arranged that the volatile products from the carbonising apparatus pass through a number of cells, either adjacent to one another or superimposed, and connected in series by means of overflow pipes, the mixture gradually becomes cooled. For reasons explained above, the main bulk of the tar separates out and collects as a liquid, filling the vessel up to a certain level and serving as a washing agent, thus bringing about further separation of tar. In the first few vessels of the series the mixture of gas and vapour is washed with tar, but in the succeeding vessels the content of tar in the washing agent steadily decreases.

During the passage of the mixture through the condensed liquid, interchange of components takes place. The products remaining in the form of vapour take up the low-boiling com-

ponent—namely, pyroligneous acid; and the high-boiling products mix with the condensed liquid.

Any tar which is carried over mechanically from one chamber to another in the form of mist becomes liquefied as a result of impact with the washing agent, and the outcome of all these different processes is that *the whole of the tarry vapours, which are always present in the mixture evolved from the retorts, are separated out in the form of liquid containing only a small amount of pyroligneous acid*, this separation being effected before the components of pyroligneous acid are condensed.

The only products carried over by the pyroligneous acid are those components of the light and heavy oils which are volatile in steam and, especially, in the presence of non-condensable gases. These products settle readily and are thus easily separated from the pyroligneous acid.

In practice this process is carried out by inserting a column composed of a series of cells—for example, a copper bell-and-tray washer specially designed to fulfil the above-mentioned conditions—between the retort and the condenser. As soon as carbonisation begins and the mixture of gas and vapour enters this apparatus, the series of processes described above takes place in the various cells. The cells must, of course, possess the right dimensions, namely, the area of air-cooled surface and the free cross-sectional area, which experience has shown to be necessary for ensuring a gradual fall in temperature from chamber to chamber, for producing a sufficient quantity of condensed liquid, and for regulating the velocity with which the gaseous mixture passes through the apparatus.

Obviously, the size of the apparatus must vary in accordance with the size of the carbonising apparatus, the performance of the latter, and the kind of wood carbonised; the correct dimensions for any particular case can only be arrived at satisfactorily as a result of practical experience.

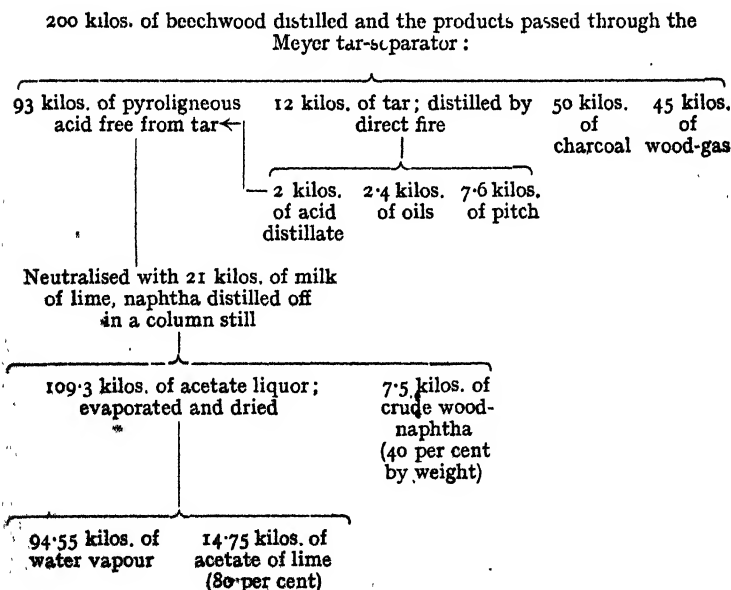
On carbonising air-dry beechwood and using the tar-separator process, the pyroligneous acid which is obtained after removal of the light and heavy oils possesses approximately the following composition:—

	Per cent.
Acetic acid and homologues	7-9
Wood-naphtha	2.5-3.2
Water	87.2-91.4
Residue on evaporation at 100° C.	0.1-0.3

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These figures indicate that the quality of the pyroligneous acid obtained directly from the carbonisation process by the use of the tar-separator is equal to that of the distilled acid produced by simple distillation of crude pyroligneous acid. It is quite feasible, therefore, to neutralise the acid from the tar-separator *directly* with milk of lime, and to work up the neutralised liquor to grey acetate of lime and wood-naphtha. In this way the cost of the steam required for the distillation of the crude acid is saved.

The following flow-sheet shows in outline the treatment of wood by the above process, which, after condensation of the tar-free pyroligneous acid, is similar to Process A. As far as the evaporation of the acetate liquor is concerned, the process can also be carried out on the lines of the vacuum process described on p. 211.



The amount of heat required theoretically for working up pyroligneous acid according to Process D is made up as follows :—

Kilo-calories.

(a) and (b) Distillation of pyroligneous acid (effected in the tar-separator without addition of heat) :	—
(c) 116.8 kilos. of acetate solution heated to boiling point; naphtha distilled off to form a 40 per cent solution :	7,888
(d) 94.5 kilos. of water evaporated from 109.3 kilos. of acetate liquor (using a vacuum apparatus, ¹ but without waste steam) :	34,200
Total per 100 kilos. of crude pyroligneous acid	42,088

If the vacuum apparatus is omitted, the total amount of heat required is 58,540 kilo-calories, as against :—

111,831 kilo-calories for Process A.	
82,771 " " " B (three-vessel).	
63,040 " " " C (vacuum apparatus).	

Thus, compared with the three-vessel process, the tar-separator process shows a saving of almost 50 per cent of fuel.

This process also offers the advantage that the whole of the tar is separated at one place and does not pass to other parts of the factory. Moreover, the retort condensers seldom require cleaning, and smaller buildings can be used to house the plant for the treatment of pyroligneous acid.

Process E.—Combination of Process D with Process B: Production of acetate liquor and dilute wood-naphtha by conducting the volatile products from the carbonising apparatus directly into mills of lime.

German patent 60,520, which was granted to F. W. Leffelman, Berleburg, on 16th June, 1901, and has now expired, dealt with the production of acetate liquor and dilute wood-naphtha directly from the volatile products leaving the carbonising apparatus, the latter, in a sense, taking the place of the first vessel of the three-vessel system.

According to the patent-claim the process consisted in passing the gases and vapours, evolved from the retorts, through a pipe, fitted with a test-cock and stop-cock, into a bell which floated on the tar in a tar pit and was provided

¹ German patent 193,382. See p. 213.

with a filter-plate and cooling pipes. After leaving the bell, the gases were conducted through a tar filter and thence into milk of lime which extracted the acetic acid. The gases then passed into a column fitted with perforated plates and provided with a reflux condenser; the liquor separating in the column collected in a chamber, from which it was run off by means of a cock into a container. By heating the liquor in the container, the methylalcohol present was driven over into the column again, through a pipe. The gases issuing from the reflux condenser were passed through a further cooling arrangement which freed them from the methyl alcohol.

Direct production of acetate liquor and dilute naphtha on the lines suggested by the above patent is undoubtedly an attractive proposition, since, according to this process, not only would it be unnecessary to condense the products as a preliminary to further treatment, but it would also be possible to utilise their latent heat and superheat for concentrating the acetate liquor and distilling off the naphtha.

The general ideas underlying Leffelmann's patent were quite sound, but they could not be realised in practice. Until the introduction of the Meyer patent tar-separator no method was successful in eliminating the whole of the tar from the gases and vapours leaving the carbonising apparatus; tar-separators constructed on the principle of the hydraulic mains employed in gasworks are certainly capable of extracting a large quantity of tar from the volatile products of wood-distillation, but not a sufficient amount to permit the production of 80 per cent acetate of lime by passing the gases and vapours leaving the tar-separator directly into milk of lime.

Treatment of the volatile products on the lines of Process D was successfully established in 1905, as a result of the introduction of the Meyer tar-separator; in the following year the author carried out a series of large-scale experiments with the object of obtaining acetate liquor and dilute naphtha by passing the mixture of vapour and gas leaving the tar-separator directly into milk of lime.

The results of these experiments seemed to point to the possibility of carrying out the process on a practical scale; it was realised, however, that a very great complication in the method of operating the carbonising apparatus would be involved. In the first place, a process of this nature would require the greatest possible regularity in the flow of vapour.

In the ordinary process of distillation the latter condition is not attained, and it would only be possible to fulfil this requirement by operating a number of retorts, each at a different stage of the process, and passing the volatile products into a single gas-main which would convey them into the tar-separator and thence into the milk of lime containers.

In this way a more uniform flow of vapour could be maintained, but at the same time difficulties would arise owing to the formation of tar-coke in the collecting main. Frequent cleaning would be necessary, and would involve the closing down of the whole plant—a grave objection for which the great advantages offered by the process scarcely compensate.

Moreover, the retorts must operate against the very considerable back-pressure set up in the milk of lime containers. Since the vapours are highly diluted by the non-condensable gases, at least two containers must be provided, and the arrangement of these vessels must be such that they can be brought into, or thrown out of, action without interrupting the process. (See Fig. 25, p. 209.)

The back-pressure mentioned above amounts to at least 2.5 metres of water; it is obvious, therefore, that unless the volatile products were drawn by suction through the milk of lime, the retorts could not work satisfactorily and could never be kept gasketed.

Hence, in order to overcome the back-pressure, powerful fans must be provided, and a considerably reduced pressure must be maintained in front of the milk of lime vessels.

The difficulties which may arise as a result of applying powerful suction in this manner have already been mentioned. If the slightest defect exists in the joints of the retort doors or in the rivets and seams of the shell, air will enter the retort and as a result the yield and quality of the acetate of lime and naphtha will be affected. Moreover, a fan which is capable of overcoming such a high degree of back-pressure will require a very considerable amount of power, thus involving extra expenditure in fuel. These examples, however, do not complete the list of disadvantages.

Certain components of the tar, namely light oils and phenols, are volatile in steam and therefore pass over with the vapours of pyroligneous acid, no type of tar-separator being capable of retaining them. In operating Process D these products are condensed with the pyroligneous acid, from

which they are separated by settling before the acid is neutralised. This method of separation, however, cannot be applied if the acid vapours, after being freed from tar, are neutralised directly; in these conditions the oils pass into the milk of lime and render the production of grey acetate of lime reaching the ordinary commercial standard much more difficult.

It will be readily understood that if any interruption should occur in the operation of the plant—for example, breakdown of the heavily loaded suction fan, blocking of the gas-main or of the milk of lime vessel, either of which is easily possible—the whole process must be affected, since the various items of plant are working interdependently.

With these facts in view it is unlikely that, except in a case of absolute necessity, anyone would be inclined to burden the process of wood-distillation with such complications, and to render it so unreliable, especially when it is possible by combining Process C with Process D to produce the same effect without introducing the complications.

Direct production of tar, acetate liquor, crude naphtha and non-condensable gases from the mixture of gas and vapour evolved from the retorts can only be carried out satisfactorily if it is possible to reduce the back-pressure, set up by the milk of lime, to such an extent that only a small reduction in pressure is rendered necessary in front of the retorts, or else in front of the absorption vessels.

On the other hand, if Process D be combined with Process C, that is, if the acetate liquor obtained in the former be evaporated in a multiple evaporator—if possible by means of waste steam or gases—to a concentration of 30 per cent, a still more efficient utilisation of waste heat is attained.

From the above considerations it is obvious that treatment of the products of wood-distillation in the form of gas or vapour immediately after they leave the retort involves serious complications, without at the same time leading to as great economy in heat as is effected by a process already in practical operation.

These facts are mentioned because the direct process, which has been known since 1891, is still often advertised as the latest and best, although even to-day it has not emerged beyond the experimental stage.

The main disadvantages attaching to Leffelmann's process are :—

1. The back-pressure set up by the milk of lime ; this can only be overcome by vigorous suction, which may easily give rise to reduced pressure in the retort itself, with serious consequences.
2. Reaction between phenols, wood-oils, etc., and milk of lime, which has a detrimental effect on the quality of the acetate of lime.
3. Frothing of the milk of lime when the pressure is reduced to any considerable extent.

An attempt was made to avoid these difficulties by extracting the acid vapours with calcium carbonate (limestone) instead of milk of lime, according to F. H. Meyer's patent process¹—most conveniently by passing the vapour through towers containing the carbonate in lumps about the size of the fist. In this way, not only is the back-pressure on the retorts almost entirely eliminated, but reaction between the neutralising agent and the phenols and wood-oils, and therefore subsequent contamination of the acetate of lime, are also prevented, since phenols do not decompose calcium carbonate and the latter shows no tendency to emulsify the wood-oils.

In carrying out this process the vapours from any type of carbonising apparatus are conducted through a tar-separator, and are then passed into a tower of suitable height, constructed of copper or other sufficiently resistant material ; in the lower portion of the tower is a perforated tray on which the carbonate is spread in a sufficiently thick layer.

Acetic acid is the only component of the mixture of gas and vapour entering the tower which reacts with the carbonate ; all other components, including the phenols and wood-oils which are volatile in steam, escape from the upper portion of the tower into a condenser. The solution of acetate of lime flows from the lower portion of the tower into a series of wooden vats ; these act as a Florentine receiver and serve to separate any traces of oils which have been carried over mechanically with the acetate liquor. In order to ensure thorough reaction between acid and carbonate the latter must be moistened, and this can be effected by means of a reflux condenser attached to the tower, or by some arrangement inside the tower for spraying the material with water, pyroligneous acid, acetate liquor, etc., or even by introducing

¹ German patent 214,558.

gases, at a lower temperature than the products from the retort, into the tower.

The products escaping from the tower consist chiefly of water vapour, naphtha, phenols, wood-oils and non-condensable gases, all of which, with the exception of the last-named, condense to form a liquid mixture. The non-condensable gases escape through a gas-separator, and can be used eventually for heating the retorts.

The condensed liquor is treated with milk of lime, and naphtha is then distilled off; the phenols, wood-oils, etc., remain combined with the lime as a valueless residue.

Unfortunately, this process has proved unsuccessful, for according to the author's experience, calcium carbonate under the above conditions never extracts acetic acid completely from the vapour passing up the tower. Consequently it is necessary to carry out the final extraction with milk of lime, and the advantages of the process are largely lost.

II. ISOLATION OF WOOD-NAPHTHA AND PRODUCTION OF METHYL ALCOHOL AND DENATURING WOOD-NAPHTHA

In Process B (three-vessel, p. 204) and Process E—if the latter be regarded as feasible—the pyroligneous acid is neutralised with milk of lime while still in the form of vapour, and a more or less concentrated aqueous solution of wood-naphtha is obtained at the same time. Processes A, C and D, however, in which the pyroligneous acid, after being freed from tar, is condensed before neutralisation with lime (or soda), furnish a solution of acetate which still contains the whole of the wood-naphtha and all precipitated matter formed during the process of neutralisation. (For details, see pp. 198-202.)

Process B (three-vessel), if applied to beechwood pyroligneous acid, produces acetate liquor containing 20-25 per cent of acetate of lime, and an aqueous solution containing 10 per cent of wood-naphtha, whereas Processes A, C and D furnish acetate liquor containing about 12 per cent of acetate of lime and only 2.5-3 per cent of wood-naphtha.

One of the most important tasks in connection with the distillation of wood is to isolate the wood-naphtha from the original dilute liquors and to concentrate the product. The

only practicable method available for this purpose is fractional distillation.

The effects of subjecting a liquid containing two or more components to fractional distillation vary widely according to the relative proportions in which the components are present, and whether or not the components are miscible; also according to the boiling points and molecular weights of the components, and their vapour pressures, at the boiling point of the mixture.

Rectification of crude wood-naphtha solutions consists in separating liquids which are *miscible*—as the term “solution” already indicates—namely, methyl alcohol and acetone on the one hand (as the most important constituents), and water or an aqueous salt-solution on the other hand.

The process should therefore obey the laws which hold good for miscible liquids possessing different boiling points. Actually, however, the conditions are not quite so simple.

Owing to the presence of methyl alcohol and acetone, other products, usually insoluble in water, are held in solution—for example, the wood-oils. As soon as the main bulk of the more readily volatile methyl alcohol and acetone has been distilled off, the wood-oils mostly separate out, and it then becomes a matter of distilling non-miscible liquids.

According to the investigations of Naumann¹ the following regularities appear in the distillation of *non-miscible* liquids—for example, water and wood oils :—

1. A constant boiling point, which is independent of the proportions in which the components are present, and which lies below the boiling point of the most volatile component.

2. A constant relationship between the weights of the components present in the distillate, depending on the molecular weights and the vapour pressures of the components.

If the boiling point of a mixture of two non-miscible liquids, the vapour pressure of each component at that boiling point and the vapour densities of the components are known, it is possible, according to the formula given by Naumann, to calculate the molecular proportions of the two components present in the distillate.

Unfortunately, these laws do not hold good for miscible liquids. A mixture of the latter usually begins to boil at a

¹ Ber., 1877, 10, 1421, 1819, 2014, 2099.

temperature which lies above the boiling point of the more volatile component, and is proportionately higher, the greater the amount of the less volatile component present.

In view of this behaviour Dossios¹ concluded that, in a liquid mixture, the total attraction exerted on the individual molecules of a volatile component is greater than the attraction exerted in the volatile component itself. If, for example, $A+B$ represents two liquids miscible in all proportions, a represents the force of attraction exerted by all the molecules of A and B on one molecule of A , and b the force of attraction exerted by all the molecules of A and B on one molecule of B , the case may occur where a is less than b .

During distillation in these conditions a greater proportion of A - than of B -molecules will escape in the form of vapour. The B -molecules will tend to concentrate in the distillation-apparatus, and since the force of attraction is greater between unlike molecules than between like molecules, a will gradually increase, b will gradually diminish. As a result, either the original relationship of a to b may still obtain, that is a always remains less than b , or the case may occur where a becomes equal to b .

The condition $a=b$, which is frequently found, renders fractional distillation quite impossible, since the composition of the distillate must then be the same as that of the residual liquid in the still.

It is due to these factors that mixtures of liquids do not always distil in the order of the boiling points of their components, but often exhibit considerable deviations owing to the influence of vapour density, vapour pressure and the molecular composition of the mixture.

In treating solutions of wood-naphtha it is chiefly a question of separating on the one hand a mixture of aldehyde, methyl acetate, acetone and methyl alcohol, and on the other hand wood-oils (higher ketones, hydrocarbons), from water.

Under a pressure of 760 mm. acetone—the most important component accompanying the methyl alcohol—boils at 56°C ., methyl alcohol at 66°C ., and water at 100°C .

When the mixture is heated, the escaping vapour contains more acetone and methyl alcohol and less water and high-boiling wood-oils than the original liquid. As distillation proceeds, the proportion of low-boiling constituents (acetone

¹ Vierteljahrsschrift der Züricher naturforschenden Gesellschaft, 1868, 12, 1.

and methyl alcohol) in the vapour gradually diminishes, the wood-oils distil over, and finally only water vapour passes into the condenser.

If the distillation be interrupted at this point, the distillate will then contain the main bulk of the acetone and methyl alcohol, and the amount of distillate will represent only a fraction of the amount of original liquid.

Hence, in order to isolate wood-naphtha from an aqueous solution, a portion of the latter must be distilled off. The relative amount of distillate depends on the amount of alcohol

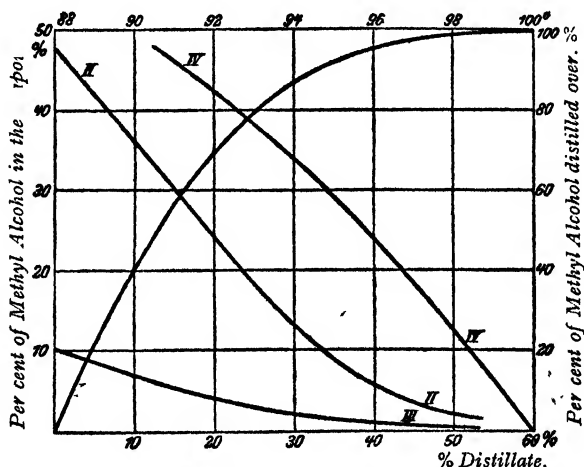


FIG. 27. DIAGRAM FOR AN AQUEOUS SOLUTION CONTAINING 10.3 PER CENT OF METHYL ALCOHOL.

originally present in the mixture. For mixtures of ethyl alcohol and water the amounts of distillate which must be produced in order to ensure the complete elimination of alcohol from the original mixture have been determined exactly.

Hilding Bergström and Oscar Fagerlind¹ have carried out similar determinations for aqueous solutions of methyl alcohol, and the results are given in Figs. 27 and 28.

The diagram shown in Fig. 27 is constructed for an aqueous solution containing 10.3 per cent by weight of methyl alcohol, and includes four curves.

Curve I, referred to the right-hand vertical axis, indicates the percentage proportion of the original total amount of

¹ Jern Kontorets Annaler, 1908, 63, 90.

alcohol (100 per cent) which is present in the distillate when the amount of the latter varies from 10 to 60 per cent of the amount of original liquid submitted to distillation.

Curve II, referred to the left-hand vertical axis, indicates the concentration of the vapour, and Curve III the concentration

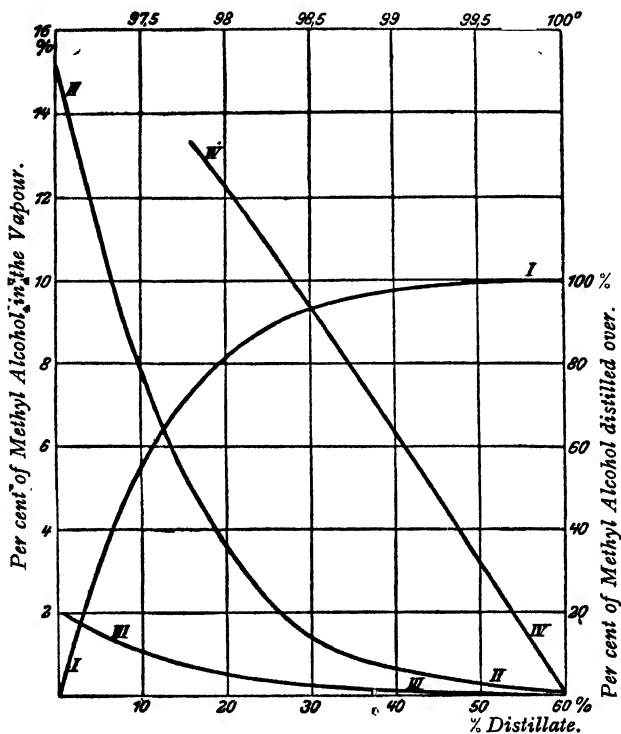


FIG. 28. DIAGRAM FOR AN AQUEOUS SOLUTION CONTAINING 2.03 PER CENT OF METHYL ALCOHOL.

of the residual liquid. Finally, Curve IV (left-hand ordinate, upper abscissæ) gives the boiling points.

Example : If a 10.3 per cent solution of methyl alcohol is distilled until the amount of distillate represents 10 per cent of the original liquid, the distillate (Curve I) will contain 40 per cent of the total amount of methyl alcohol submitted to distillation ; the vapour will contain 36 per cent of alcohol (Curve II) ; and the residual liquid (Curve III, left-hand ordinate) at this point will contain 7 per cent of alcohol.

Curve IV gives the boiling point of the liquid, namely, 93.4°C .

The diagram shown in Fig. 28 is constructed on exactly the same principle, for an aqueous solution containing 2.03 per cent of methyl alcohol, and the curves have the same significance.

On the basis of these diagrams Bergström and Fagerlind have also compiled the following tables:—

BOILING POINTS AND CONCENTRATION OF VAPOUR FOR
METHYL ALCOHOL SOLUTIONS OF VARIOUS
CONCENTRATIONS

Boiling point. °C.	Per cent of methyl alcohol in		Boiling point. °C.	Per cent of methyl alcohol in	
	the original solution.	the vapour.		the original solution.	the vapour.
90.90	10.0	46.8	98.82	1.0	7.4
91.70	9.0	43.1	98.94	0.9	6.7
92.60	8.0	39.7	99.07	0.8	5.9
93.40	7.0	36.3	99.18	0.7	5.2
94.30	6.0	32.6	99.29	0.6	4.5
95.10	5.0	28.6	99.41	0.5	3.8
96.00	4.0	23.8	99.54	0.4	2.9
97.00	3.0	18.8	99.66	0.3	2.2
97.70	2.0	14.8	99.79	0.2	1.3
98.40	1.5	11.7	99.90	0.1	0.6

DISTRIBUTION OF METHYL ALCOHOL ON DISTILLATION FROM
AQUEOUS SOLUTIONS

Amount of distillate, expressed as per- centage of the original solution.	Amount of methyl alcohol in the distillate, ex- pressed as percentage of the total amount present in the original solution, when	
	Concentration of original solution = 10 per cent.	Concentration of original solution = 2 per cent.
10	40.0	55.0
20	65.0	82.0
34	87.0	93.0
40	95.0	95.0
50	98.6	99.4
60	99.6	99.9

For example, if 34 per cent of a 10 per cent methyl alcohol solution is distilled off, 87 per cent of the methyl alcohol originally present in the solution will be found in the distillate.

At the outset the concentration of the vapour obtained from a 10 per cent solution of methyl alcohol is about 4.7 times as great as that of the original solution; from a 5 per cent solution it is about 5.7 times, and from a 2 per cent or weaker solution about 7.4 times as great.

In order to obtain concentrated alcohol from a weak aqueous solution, the first distillate must therefore be re-distilled, and this process must be continued until the desired concentration has been reached.

Ethyl alcohol cannot be concentrated beyond 97 per cent by volume without the assistance of dehydrating agents (lime, etc.), but with methyl alcohol it is possible to reach a concentration of 99 to 100 per cent by fractional distillation alone.

Formerly, the process of concentrating dilute solutions of wood-naphtha was carried out exactly as indicated above, by producing from, say, a 3 per cent solution a 6 per cent distillate by the first distillation, then a 12 per cent solution from the latter; then by further distillation possibly a 30 per cent distillate, from the latter a 50 per cent distillate, and so on.

This method of operation, involving as it did a large number of separate distillations before a sufficiently high concentration was obtained, can scarcely be regarded as simple. It was quickly abandoned after the column stills, by means of which it is possible to produce concentrated alcohol in one single operation, had been introduced into the wood-distillation industry.

The working principle of modern rectifying plant is based entirely on that of the old, simple type of apparatus, which consisted merely of a pot-still and a condenser.

The process of rectification in column stills, as carried out in practice, is best illustrated by the arrangement shown in Fig. 29, in which a vessel A, representing a pot-still, is combined with a number of considerably smaller vessels B-I arranged terrace-wise above the first vessel and connected among themselves and with the first vessel by vapour delivery pipes and overflow pipes. A condenser F completes the

ern. The solution of alcohol which is to undergo concentration

(the alcohol content is a matter of indifference) is introduced into the vessel A and raised to boiling by some suitable form of heating arrangement. As stated above, the vapour escaping from an alcohol-water mixture is always richer in alcohol than the liquid from which it is derived. On passing through the vessels B-D, which at the outset are cold and empty, the vapour evolved from A is cooled by the walls of the vessel, and condenses, forming a distillate which is substantially richer in alcohol than the original mixture in A. By the action of the water and alcohol vapours coming over from A, a vapour mixture still richer in alcohol is evolved in turn from the condensed liquid in B to form a distillate in C. The condensed liquid in C evolves still more highly concentrated vapour which passes into D.

It is obvious that, if a sufficient number of small vessels were employed in combination with the first vessel, it would be possible in this manner to isolate alcohol in concentrated form from dilute aqueous solutions in a single operation, the process consisting in raising the dilute solution to boiling, condensing the vapour mixture evolved, and submitting the successive distillates to the same treatment as the original solution.

Naturally, a sufficient quantity of condensed liquid can only be formed in B, C and D as long as these sections of the apparatus still remain cold and it is possible, therefore, for the vapours passing through the system to transfer heat to the walls of the vessels. As soon as the temperature of the latter reaches that of the vapour, continued production of condensed liquor in sufficient quantity is out of the question, since the loss of heat by radiation from copper surfaces is only small—namely, about 3 kilo-calories per 1 sq. metre per hour for a temperature difference of 1°C .

It follows, therefore, that after the apparatus has been in operation for a short time condensation will gradually diminish, the individual vessels will assume approximately the same temperature, and fractionation can no longer take place.

If air-cooling alone were relied upon to produce sufficient amounts of condensed liquor from a mixture of alcohol and water vapours, it would necessitate the provision of very large vessels for the system. In concentrating aqueous solutions of alcohol, however, the aim must be to produce the condensed liquor, not at one point only, but at as many separate points as possible, and at each of the latter only in relatively small

amount; it is impossible, therefore, to employ air-cooled plant of such large dimensions for this purpose.

A rectifying plant can only be looked upon as practicable if it is capable of fulfilling the above requirements without having to rely on air-cooling.

Suppose that each of the vessels B-D in Fig. 29 were fitted with a water-cooled reflux condenser, then the apparatus

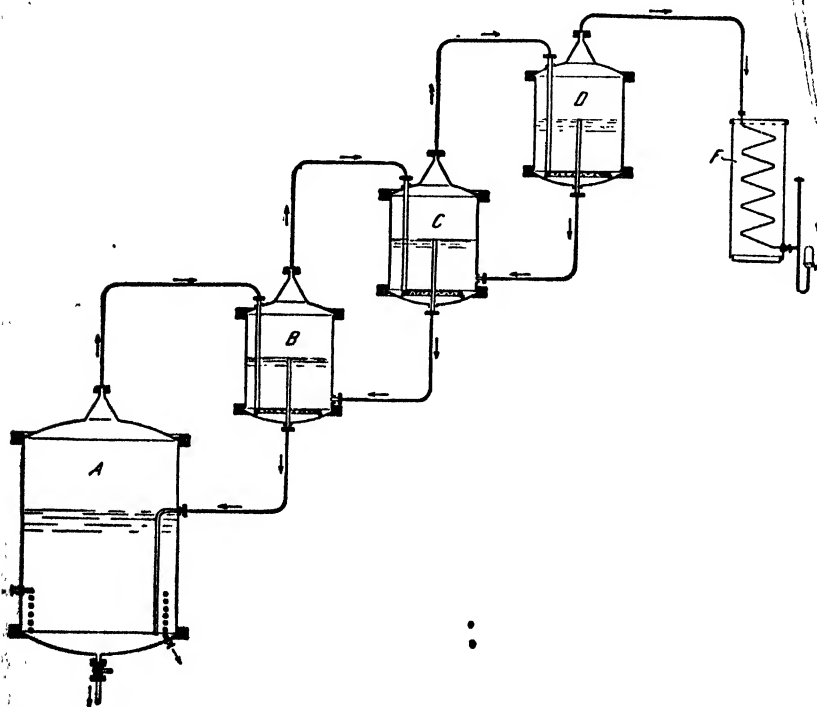


FIG. 29.—ARRANGEMENT ILLUSTRATING THE ACTION OF A COLUMN STILL.

would meet all requirements mentioned above. It would permit uniform production of condensed liquor during the whole period of operation; it would produce condensed liquor at a large number of separate points and in relatively small quantities; and it would operate on the counter-current principle, since the products rich in alcohol would flow towards the condenser F, whereas the products containing relatively

little alcohol would travel by way of the overflow pipes towards the vessel A. The vapours evolved from A would be partially or wholly condensed in B by the action of the condenser *b*. As the vapour continued to pass over from A it would generate a vapour mixture richer in alcohol from the condensed liquor in B; this mixture in turn would undergo condensation in the condenser *c*, producing condensed liquor in C, and so on.

An apparatus of this kind already contains all the elements of a modern column still.

If, however, we realise that in order to isolate methyl alcohol in concentrated form (96-100 per cent) from aqueous solutions, we should require from twenty to forty of these small vessels and an equal number of condensers, according to the initial strength of such solutions, it will be obvious that an apparatus which is so complicated and would naturally require much attention is totally unsuited to actual practice, quite apart from the disadvantage that it would occupy very considerable space.

We have seen that rectification can only be effected by a process of repeated condensation and vaporisation; further, that air-cooling is impracticable, and that the introduction of water-cooled condensers, between the separate vessels in which the condensed liquor is produced, renders the system too complicated.

The next step towards a perfect type of rectifying apparatus is the introduction of the principle of "wet condensation" for the purpose of producing condensed liquor in the separate vessels or, to use a simpler term, the "cells."

If we assume that the temperature of the liquid in B is 95° C., corresponding to the boiling point of a solution relatively weak in alcohol, and that of the liquid in the last vessel D is 66°, corresponding to the boiling point of concentrated methyl alcohol, it follows that we should be able, step by step, to cool down the liquid contained in the separate "cells" B-D by allowing a sufficient quantity of the liquid in D to return through the overflow pipes towards A, and therefore to produce condensed liquid in any quantity desired.

In passing from D to A this cooling liquid, which consists of highly concentrated alcohol, performs a second task which consists in increasing the alcohol content of the liquid contained in the separate cells. The higher the concentration of

alcohol in this liquid and the richer the vapours, the smaller is the number of cells required.

Suppose that the apparatus is now arranged in the following manner: A reflux condenser is attached to the last cell only

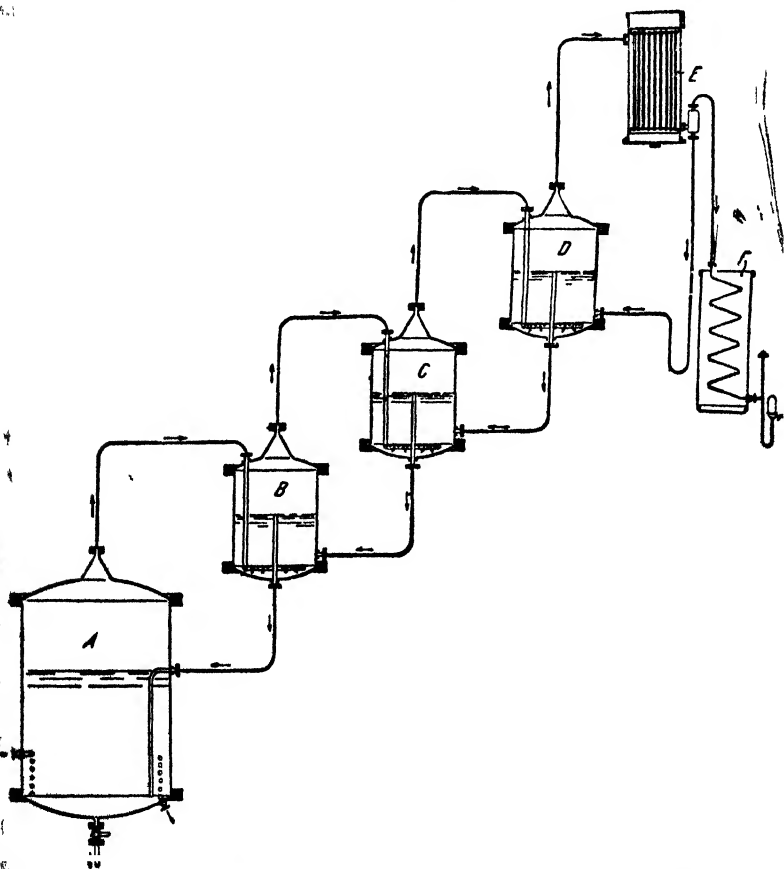


FIG. 30.—THE ELEMENTS OF A COLUMN STILL REPRESENTED AS A SYSTEM OF DISTILLATION VESSELS.

(see Fig. 30); in order that a sufficient quantity of cooling liquid shall be produced, provision is made for repeated vaporisation of the cooling medium passing back through the overflow pipes to A; and finally the cells, instead of being arranged terrace-wise, are superimposed to form a vertical system

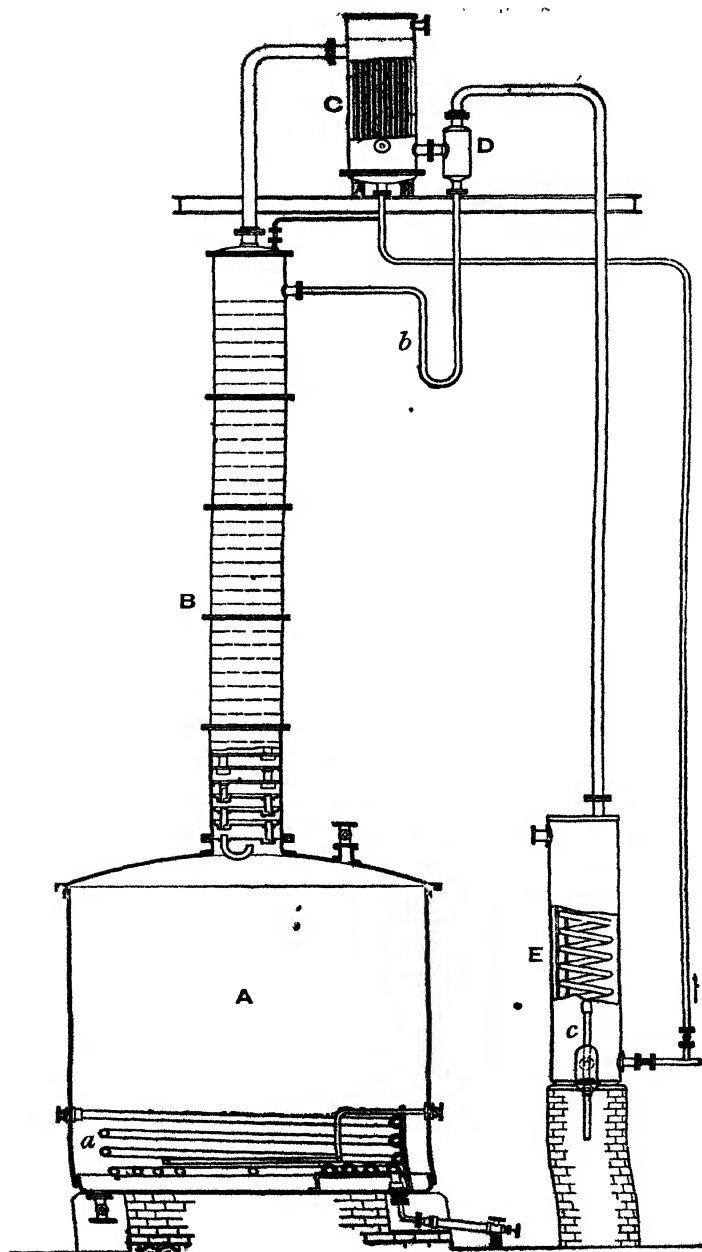


FIG. 31.—DIAGRAM SHOWING THE CONSTRUCTION OF A MODERN COLUMN STILL FOR INTERMITTENT OPERATION.

"column." We should then have an apparatus possessing the essential features of a modern column still.

The complete apparatus consists of a vessel of any suitable form and material, heated in any suitable manner; it supports a vertical "column" composed of cells which are connected in series by means of overflow pipes; the latter also regulate the level of the liquid in the cells. Above the column is the reflux condenser—also termed the "dephlegmator" or, erroneously, the "separator"—in which the liquid acting as cooling agent is produced; the temperature of this liquid is usually kept near its boiling point. The reflux condenser is connected with an ordinary condenser, which serves to condense a portion of the finished product issuing from the dephlegmator in the form of vapour.

Fig. 31 shows a modern column-still embodying the above

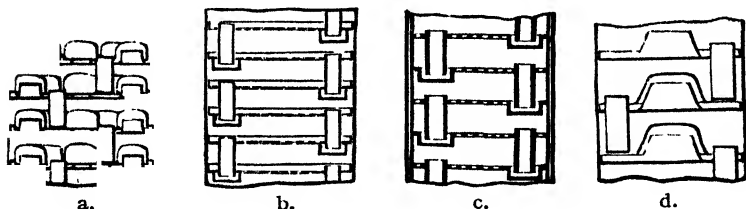


FIG. 32.—DIFFERENT FORMS OF FRACTIONATING PLATE USED IN THE COLUMN.

principles and designed for intermittent rectification of dilute wood-naphtha.

The main details of this apparatus comprise the vessel A fitted with a steam-coil *a*, the column B, the reflux condenser or dephlegmator C connected with the separating-chamber D and provided with a return pipe *b*, and the condenser E with an aerometer outflow *c*. The naphtha vapours, already enriched by the first vaporisation, pass directly from the vessel A into the column B, in which the process of frequently repeated condensation, followed immediately by re-vaporisation, takes place automatically. The internal fittings of these columns vary widely in form.

Some of the more important types are shown in Figs. 32a-d. The forms most commonly employed in practice are the perforated plates (Fig. 32b), and the bells and trays (Fig. 32a);

the details of construction are obvious from the diagrams. Compared with the perforated plates the bell-and-tray arrangement has the advantage of being less affected by accidental diminution in the supply of vapour.

The cells are so arranged in the column that the overflow- or drip-pipe belonging to one plate always dips into the bowl of the next lower plate (cf. Figs. 32b and 32c); the drip-pipes and bowls are therefore set alternately throughout the entire column.

The wood-naphtha vapour rising from below passes through the first plate and travels thence from plate to plate

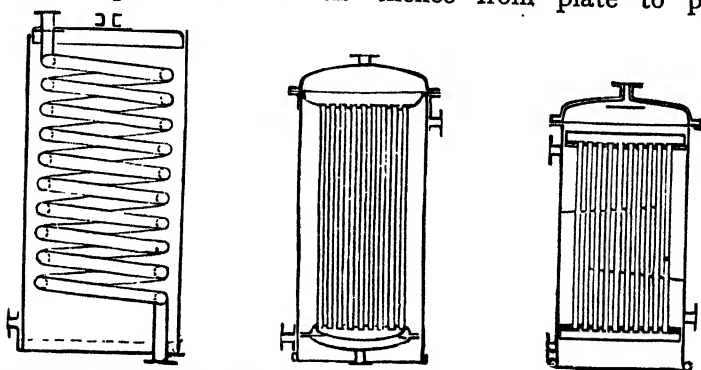


FIG. 33.—VARIOUS FORMS OF REFLUX CONDENSER (DEPHLEGMATOR) USED ON COLUMN STILL.

throughout the column, finally leaving the uppermost cell and entering the reflux condenser C. The latter is usually a tubular condenser (see Fig. 33) which condenses the greater part of the incoming vapour and returns the condensed liquid, through a siphon-pipe *b* of suitable length, to the top plate of the column, which becomes covered with a layer of liquid about 2 cm. in depth, corresponding to the height to which the drip-pipe projects above the plate. As soon as the layer reaches this height, the liquid begins to overflow down the drip-pipe on to the second plate (reckoned from above), and the flow continues from plate to plate and finally back into the vessel. After the evolution of vapour from the vessel has been in progress for a short time, each plate is covered with a layer of liquid; in the case of perforated plates the layer is supported by the ascending vapours which, in passing through the liquid, convert a portion of the latter into vapour.

During distillation, therefore, the internal space of the column is occupied by an ascending stream of vapour and a descending stream of liquid, the latter being produced as a result of the action of the reflux condenser.

The ascending vapour is condensed in the first place on the bottom plate, the condensed liquor is partially vaporised, further condensation takes place on the second plate (reckoned from below), and so on, until, as a result of this process of repeated vaporisation and condensation, the top plate becomes covered with liquid. The vapour rising from the top plate passes into the reflux condenser, in which at first it is completely condensed. But in proportion as the inflowing vapour heats the water surrounding the walls of the condenser, condensation is no longer complete: in consequence, a portion, consisting of the more highly volatile products, passes through the separating-chamber D into the main condenser E, where it becomes condensed and cooled, to appear finally as the distillate. The hot condensed liquid produced by the condensation of the main bulk of the vapour in the reflux condenser flows back to the top plate of the column, and thence downwards from plate to plate, thus maintaining the layers of liquid on the plates at a constant level. In the course of its descent, however, this condensed liquid, which is rich in alcohol, enriches the layers of liquid on the plates, and therefore the ascending vapours, with alcohol. In this manner every portion of wood-naphtha which is finally obtained as distillate from the main condenser undergoes repeated vaporisation, condensation and re-vaporisation, according to the number of plates present in the column and the number of times it passes up and down the column.

This brief explanation of the process is sufficient to indicate the importance of the part played by the reflux condenser in the operation of a column still. In order to obtain a definite quantity of distillate per hour at a definite degree of purity, it is always necessary that in the same period a larger but definite quantity be repeatedly vaporised, passed through the column, and returned by the action of the reflux condenser. For this reason the performance of a column still is not only governed by the size of the heating surface effecting the initial vaporisation, and the size of the cooling surface effecting reflux condensation, but it is also dependent on the cross-section of the column itself and of the drip- or overflow-pipes. Unless

these factors harmonise, the rectifying apparatus will not perform its duty.

Even supposing that the apparatus has been skilfully constructed and, therefore, all the essential parts of the plant bear correct relations to one another, in order to be in a position to obtain satisfactory yields of saleable products from the crude material at the greatest possible rate, it is still necessary to establish the most favourable working conditions for each individual apparatus when it is first brought into operation, and to provide special means for indicating these conditions to the operator. Thus, the correct supply of steam may be indicated by marks on a pressure gauge or notches on the steam valve; or, again, the valve may be fitted with a graduated dial-plate and pointer. Similarly, the water supply to the dephlegmator may be controlled by means of a gauge, and a dial and pointer on the water cock, and also by measuring the temperature of the hot water leaving the dephlegmator. Moreover, an expert distiller is able to recognise whether or not the proper amounts of steam and water are being supplied, from the concentration of the distillate as indicated by the alcoholometer immersed in the condenser outflow.

The vessel itself is also frequently provided with a water manometer which indicates the pressure prevailing in the apparatus, the pressure depending on the amounts of steam and cooling water which are being supplied at the time. This instrument will afford exactly the kind of assistance necessary to give a new operator confidence in the management of the plant, provided, of course, that steps have been taken at the outset to ascertain definitely at what pressure, as indicated on the manometer, the best results are obtained, assuming that the quantity and quality of the charge remain constant. A steam-regulator, which regulates the supply of steam to the vessel, forms a further important item in the equipment of a modern column still.

As already mentioned above, the liquor coming forward for rectification consists either of the aqueous solution containing about 10 per cent of naphtha from Process B (p. 204) or of acetate liquor containing up to 3 per cent of naphtha from Process A, C or D (pp. 200, 211, 219).

The object of rectification is to isolate the wood-naphtha from these solutions in a concentrated and saleable form.

The term "wood-naphtha" is really understood to refer,

not to pure methyl alcohol, but to a mixture consisting of aldehydes, methyl acetate, ammonia, amines, acetone and other ketones, methyl alcohol, allyl alcohol, "wood-oils" and water.

In commerce it is usual to recognise the following different grades of wood-naphtha :—

1. *Crude wood-spirit*, which still contains all the above-mentioned components with the exception of "wood-oils." This product usually consists of about 75 per cent by weight of wood-naphtha and 25 per cent of water; it varies in colour from water-white to dark brown, but is sufficiently free from wood-oils to form a clear solution on the addition of water.

2. *Partially refined*, water-white grades of wood-spirit, which contain about 95 per cent of wood-naphtha components, but from which the amines, ammonia, possibly a portion of the acetone and allyl alcohol (as, for example, in English denaturing wood-spirit), and practically the whole of the wood-oils, have been eliminated. This group includes all varieties of wood-naphtha used for denaturing ordinary alcohol, as specified by the Governments of the different countries.

3. *Completely refined* qualities of wood-spirit, which contain 98–99·5 per cent of wood-naphtha components, and consist of almost pure methyl alcohol. The acetone content—the best standard of purity—is only 0·01–0·5 per cent; the products no longer decolourize bromine water; they are, in a certain sense, stable to permanganate, and on treatment with concentrated sulphuric acid exhibit only a more or less yellow coloration.

The methods employed for the rectification of the dilute aqueous solutions of wood-spirit, or the solutions still containing calcium acetate, differ entirely according to whether the object is to produce crude wood-spirit only or, in addition, the partially or completely refined grades.

In small wood-distillation factories it is usual, unless some special local conditions favour a different course, to limit the process of rectification to the manufacture of crude wood-spirit, the nature of which is described above; this product is exported in large quantities from the United States and Hungary.¹

¹ Most of the English factories carry the process of rectification far enough to produce miscible wood-naphtha (60 O.P.) conforming to the British Government specification (see p. 432). The "heads" and "tails" from the process of rectification are usually mixed to form a product which is not completely miscible with water and is sold as "solvent wood-naphtha."

For the production of crude wood-spirit from the 10 per cent or 3 per cent solution (the latter still containing calcium acetate) the dilute liquor is charged into the boiling-vessel of a column still. A small quantity of milk of lime is added for the purpose of saponifying methyl acetate which, as a rule, is still present, and of forming non-volatile calcium compounds with the phenols and wood-oils. The still is then started up. As soon as the distillate appears at the outlet of the condenser, the supply of steam to the still and the supply of water to the condenser are adjusted in such a manner that the distillate comes off at the highest possible concentration, and at a rate corresponding to the hourly performance of which the still is capable.

The first portion of the distillate (equivalent to about 10 per cent of the original charge) comes over with a concentration apparently below 95 per cent, since, together with a relatively large proportion of acetone, it contains certain other products—especially methyl acetate—which raise the specific gravity. The strength of the distillate rises gradually to 97 per cent and falls again towards the end of the process. Distillation is continued until the specific gravity of the distillate has risen to 1.000, thus indicating that the process is complete.

The first portion of the distillate, which contains the greater part of the acetone and seldom shows a concentration of more than 95 per cent by weight (measured with the Richter alcoholometer), is known as "*first runnings*." The portion which shows an average strength of about 97 per cent by weight, and contains a relatively small amount of acetone and other products accompanying methyl alcohol, is called "*middle runnings*." Everything coming over towards the end of the distillation at a concentration below 90 per cent down to about 50 per cent is known as "*last runnings*." The last portions of all, which mostly contain very little methyl alcohol (5-6 per cent), are usually known as "*tails*."

If the treatment is for crude wood-spirit, which is only required to show a specific gravity of 0.863 at 15° C. (80 per cent by volume, or 73.5 per cent by weight) and to be miscible with water, then the "*first runnings*" and "*middle runnings*" are collected as one fraction, and even the "*last runnings*" and the "*tails*" may be mixed with the distillate as long as the finished product does not fall below the specified limit of concentration.

In this case one, or at the most two, vats suffice for the collection of the distillate.

Crude wood-spirit with a strength of 80 per cent by volume (73.5 per cent by weight), such as comes on the market from America, should show the following approximate composition :—

	Per cent.
Acetone	12-14
Methyl alcohol	50-55
Aldehydes, methyl acetate, amines, higher ketones, allyl alcohol, wood-oils, and other products which affect the specific gravity	5-10
Water	26-28

The crude wood-spirit exported from Austria-Hungary usually shows a higher concentration (about 95 per cent by volume) and contains a smaller proportion of worthless by-products.

The American crude wood-spirit comes on the market in wooden barrels of about 50 gallons capacity, which are coated internally with size. The chief market for this product is Germany, where it is worked up in special refineries into pure methyl alcohol—for use in the aniline dye industry and for the manufacture of formaldehyde—and into the different qualities of denaturing wood-spirit.

Starting out with an aqueous solution containing 10 per cent of wood-naphtha there is no difficulty in obtaining finished crude wood-spirit (80 per cent by volume) by a single distillation in an intermittent still; this is no longer practicable, however, with acetate liquor containing only 3 per cent of wood-naphtha.

Rectification of such weak solutions in one single operation would entail not only a considerably greater consumption of steam, but also the provision of very tall columns which would substantially increase the cost of the plant. These factors would not necessarily rule out the process as unsound, if the results were at least equal to those obtained by rectifying a 10 per cent solution. It is found, however, that wood-naphtha solutions of such low concentration produce relatively large quantities of "last runnings" and "tails" which must be returned repeatedly to the process. This involves loss of material, increased charges for fuel and labour, and less efficient utilisation of the plant.

In the United States, where Process A (p. 200) is the one most usually adopted, and, as a consequence, the 3 per cent or even weaker solutions of wood-naphtha are obtained, an attempt is made to avoid these difficulties by treating the acetate liquor containing the wood-naphtha first of all in a simple distillation plant known as a "*lime-tees still*," which consists of an iron vessel connected with a condenser and heated by means of a steam-coil. The wood-naphtha is distilled off, and an aqueous distillate containing 10-12 per cent by volume of naphtha is obtained; this distillate on subsequent rectification in a column still furnishes the wood-spirit of commerce.

This method certainly gives satisfactory results, but it can scarcely be regarded as simple. Here again, the wood-spirit must be treated by two successive intermittent processes, and as a result practically the same disadvantages obtain as in direct rectification in a column still specially constructed to deal with very weak solutions.

The occurrence of "last runnings" and "tails" is naturally a phenomenon of intermittent rectification only.

If, for example, a 10 per cent solution of wood naphtha is distilled in an intermittent column still, it is obvious that the concentration of the charge in the boiling-vessel cannot remain constant. As distillation proceeds, the naphtha content of the residual liquor diminishes continually, until finally a point is reached at which the functions of the apparatus cease—in other words, water vapour alone escapes from the vessel, enters the column, and drives the wood-naphtha, still remaining on the plates, up the column and over into the condenser.

This process does not take place suddenly, but gradually, and is responsible for the occurrence of "last runnings" and "tails" during the rectification of wood-spirit. The smaller the capacity of the vessel, and the weaker and smaller the charge, the more rapidly do the contents reach the critical point, and the larger are the amounts of weak unfinished products which come over towards the end of the operation.

Rectification of wood-spirit without production of "last runnings" and "tails" is only possible, therefore, if the composition of the liquid in the boiling-vessel can be kept constant—a condition which cannot be fulfilled with a column still designed for intermittent operation.

This condition is fulfilled, however, by all column stills.

which are capable of *continuous* operation. In this type of plant the dilute aqueous solution of naphtha is not worked up in a series of separate charges, but is supplied to the still in a continuous stream and only at such a rate that the amount of liquor entering the still is equivalent to the amount of naphtha taken off as distillate.

During the whole period of operation, equilibrium is maintained between the inflowing and outflowing quantities of naphtha; moreover, the water or acetate liquor from which the naphtha has been driven off is discharged continuously by the apparatus. In these conditions the process no longer resolves itself into a series of different phases, hence neither "last runnings" nor "tails" are produced. From start to finish the only products leaving the still are a distillate of uniform composition, namely concentrated wood-naphtha, and the residual liquor free from naphtha, namely water or calcium acetate solution. Between the points of exit of these two products the intermediate products collect, likewise at quite definite points; they do not leave the apparatus, however, and both the amount and composition of these products remain constant.

The phenomena of continuous distillation will be better elucidated and explained by considering the construction and operation of a continuous column still.

The still designed for the continuous production of crude wood-naphtha from dilute aqueous solutions is shown in Fig. 34.

The dilute feed-liquor enters the still through the siphon-pipe D and flows on to the top plate of column A.

We will assume that the chamber B is filled with boiling water or acetate liquor, which is being heated by the steam-coil or possibly by direct steam.

As it flows on to the top plate, the feed-liquor meets the current of steam rising from B, by which it is likewise heated to boiling.

In accordance with the laws already stated, the feed-liquor gives off vapour which is richer in alcohol than the liquor itself. This vapour passes to the lowest plate of the concentrating column E, where the process is repeated—that is, the vapour is first of all condensed either by the cold plate or, at a later stage, by the liquid returning from the reflux condenser F; the condensed liquid is again raised to boiling by the vapour ascending from B, and gives off vapour which is

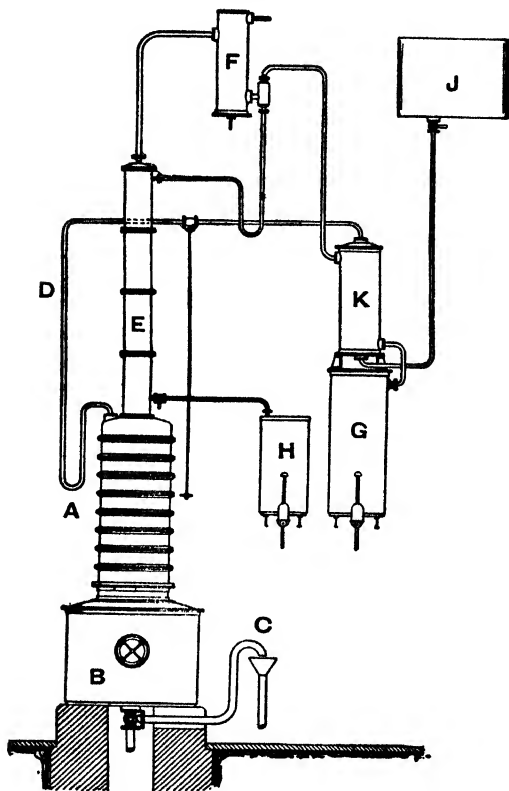


FIG. 34.—CONTINUOUS COLUMN STILL FOR DIRECT PRODUCTION OF CONCENTRATED WOOD-NAPHTHA FROM DILUTE AQUEOUS SOLUTIONS.

- A. The bell-and-tray boiling column, in which the naphtha is driven off from the dilute feed-liquor.
- B. The heating-chamber, which contains the steam-coil for heating the apparatus and regulates the discharge of naphtha-free liquor maintained at constant level in the chamber.
- C. The adjustable outlet siphon-pipe.
- D. The inlet siphon-pipe for supplying the feed-liquor to the still.
- E. The concentrating or rectifying column receiving the vapours ascending from A.
- F. The reflux condenser or dephlegmator.
- G. The main condenser or cooler for the distillate.
- H. Condenser for wood-oils taken off from column E.
- J. The feed-tank supplying the dilute solution of naphtha to the still.
- K. The preheater for the feed-liquor, heated by the concentrated naphtha vapour from F.

richer in alcohol than the liquor from which it is derived. This process goes on continuously, until finally the vapour, which by this time consists almost entirely of wood-naphtha, reaches the top plate of the column E.

Of the total amount of vapour leaving the top plate, only a very small proportion passes to the main condenser G and leaves the apparatus as the finished product (crude wood-spirit). The main bulk condenses in the reflux condenser F and returns as liquid, at the temperature of the boiling-point of wood-naphtha, to the column E, to act in the latter as a cooling agent.

The continuous still demonstrates better than any other form of column still that the reflux condenser does not act as a concentrating apparatus, but merely serves to furnish the cooling agent which brings about repeated condensation (followed by re-vaporisation) of the vapours ascending the column; that this apparatus plays no other part is proved by the fact that the product entering the condenser in the form of vapour possesses approximately the same composition as the product returned by the condenser in the form of liquid.

At the point where the feed-liquor enters the column A a process of partition is therefore taking place; vapours, richer in naphtha than the feed-liquor from which they originate, pass upwards into the column E; liquid, which has already been deprived of a certain amount of naphtha on the top plate, flows downwards from plate to plate, meeting vapours containing successively smaller proportions of naphtha, and in the end water vapour alone; finally, the liquid flows out of chamber B completely deprived of naphtha.

Owing to its refluxing action, column E also contributes to the volume of liquid passing down column A.

Hence, after a state of equilibrium has become established, the plates of column E, which lie above the feed-liquor inlet, are covered with solutions of wood-naphtha which exhibit a steady increase in strength from below upwards—say, from 20 per cent on the bottom plate to 95 per cent on the top plate; these conditions persist as long as the composition of the feed-liquor, the pressure of the heating steam, the temperature of the cooling water for the reflux condenser, and the rate of supply in each case remain unchanged.

Similarly, the plates of column A, which lie below the feed-liquor inlet, are covered with liquid which from above down-

wards exhibits a steady decrease in naphtha content, and on the lowest plate, or even before, consists only of water or acetate solution. In this case the concentration falls, step by step, from about 10 per cent on the top plate to zero on the bottom plate.

Once equilibrium is established (in one to two hours after starting up, provided that the above-mentioned factors do not vary), each plate in the apparatus—except, of course, the lowest—is covered with a solution of wood-naphtha of perfectly definite composition; moreover, the associated products, such as “wood-oils,” collect at certain definite zones in the apparatus, from which they can be removed.

It will be obvious that if feed-liquor of constant composition is supplied to the apparatus at a uniform rate, if a distillate of uniform composition is taken off at a uniform rate, and if the other above-mentioned factors remain unchanged, no variation will occur in the character of the distillate throughout the operation of the still, and the appearance of a concentrated distillate at the beginning and a weak distillate at the end, as in the intermittent process, is impossible.

Hence, a continuous column still of the type described above produces no “first,” “middle” or “last runnings,” but only a single distillate which consists of concentrated wood-naphtha.

The wood-oils, which in the intermittent process mostly come over with the “last runnings” and the “tails,” are only slightly soluble in dilute solutions of alcohol; consequently, they separate out either above or below the latter, and can be removed mechanically.

In the continuous process the wood-oils find their way into the distillate, unless special measures are taken to eliminate them from the apparatus.

The wood-oils are insoluble in water and also in dilute aqueous wood-naphtha; consequently, on distillation, a mixture of wood-oils and water (or dilute naphtha) obeys the laws quoted above for two non-miscible liquids.

According to the proportions in which water, wood-naphtha and wood-oils are present in a mixture, the wood-oils will play the part either of “first runnings” or of “last runnings” towards the other two components—“first runnings” if the proportion of water (or dilute wood-naphtha) is considerably greater than the proportion of wood-oils; “last runnings” under

opposite conditions. A third possibility, which has already been considered in connection with the phenomena of distillation, also exists, namely, that a mixture of water, wood-naphtha and wood-oils in certain definite proportions—maximum concentration of wood-oils—may assume a constant boiling-point ($a=b$, p. 230); in these conditions separation is quite impossible.

We have seen above that, in normal operation, a liquid of constant composition exists on every plate.

Accumulation of wood-oils cannot take place in the lower column, since water is always the preponderating component in that part of the apparatus; the wood-oils therefore act as "first runnings," and pass into the column E. In the latter, gradual concentration of wood-naphtha and wood-oils takes place at the expense of the third component—water—which passes into column A.

In column E the wood-oils change their rôle—in other words, they act as "last runnings," and collect as such in a definite zone of the column, remaining there until the maximum concentration mentioned above is reached, in short, until the mixture assumes a constant boiling-point; the wood-oils then gradually pass up the column and finally come over with the distillate.

From the above considerations it will be obvious that continuous production of saleable wood-naphtha, practically free from wood-oils, can only be ensured if the latter are removed from the zone in which they reach the critical degree of concentration ($a=b$). This task is performed by the condenser H, the best position of which must be determined by experiment.

The above details will suffice to illustrate the mode of operation of the modern types of continuous column still, which have become more and more widely adopted by the wood-distillation industry in recent years.

Compared with the intermittent still, the continuous still offers further advantages, apart from the fact that saleable products may be obtained in a single operation and without simultaneous production of "last runnings" and "tails." It occupies a relatively smaller amount of space, therefore the capital outlay on buildings is less; very little labour is required to operate it; and it consumes a less quantity of steam, owing partly to the absence of intermediate

products which require repeated rectification, and partly to the possibility of preheating the feed-liquor free of cost. Preheating may be carried out in various ways: for example, by means of exhaust steam; by using the liquor as the cooling agent either in the main condenser or in the reflux condenser; or by means of the hot residual liquor (water or acetate solution) leaving the apparatus. As a result of preheating alone, the saving in steam amounts approximately to 20 per cent.

In short, the numerous advantages offered by the continuous crude-naphtha still completely justify the preference which has been shown for this type of apparatus in recent years.

Crude wood-spirit, which is miscible with water in all proportions and contains all the characteristic components (methyl alcohol, acetone, aldehydes, amines, ammonia, higher ketones, esters and allyl alcohol), serves as raw material for the manufacture of the remaining commercial products, namely the various qualities of wood-spirit more or less rich in ketones, which are used for denaturing purposes and are known as "*denaturing wood-spirit*"; also *pure methyl alcohol*, practically free from acetone, and intended for use in the production of aniline dyes, the preparation of perfumes, and the manufacture of formaldehyde.

Manufacture of Pure Methyl Alcohol.—It is impossible to manufacture pure methyl alcohol from crude wood-spirit without producing denaturing wood-spirit at the same time. Consequently, it is a matter of great relief to the refineries which manufacture pure methyl alcohol that a wood-spirit product rich in acetone, and usually containing allyl alcohol, is authorised by the different countries for use as a denaturing agent for industrial ethyl alcohol.

Acetone and allyl alcohol are always present in wood-spirit. Neither of these components can be isolated in a pure saleable form from methyl alcohol at a reasonable cost. Hence, in manufacturing pure methyl alcohol from crude wood-spirit it is always necessary to take off a certain amount of methyl alcohol with the acetone and allyl alcohol fractions respectively, in order to separate these components from the main bulk of the methyl alcohol.

In this process the mixture of acetone and methyl alcohol appears as "first runnings," and that of allyl alcohol and methyl alcohol as "last runnings." These products, when

mixed in accordance with the specifications issued by the different countries, form the basis of denaturing wood-spirit.

It follows, therefore, that a refinery is practically never concerned with the question of isolating methyl alcohol alone from a given quantity of wood-spirit.

Numerous statements may be found in the literature according to which it should be possible to manufacture pure methyl alcohol from crude wood-spirit by treating the latter with suitable substances which will react directly with the acetone, for example, chlorine or iodine, or will form addition compounds with acetone or methyl alcohol, for example, sodium hydrogen sulphite or calcium chloride.

The author is able to state with certainty that methods of this kind are nowhere employed in practice and, apart from the original trials, probably never have been employed.

It is impossible to destroy the acetone by chemical treatment without losing a portion of the methyl alcohol at the same time; it is also impossible to bring about quantitative conversion of the acetone into addition compounds. Moreover, no manufacturer is willing to destroy acetone, which has a higher value than methyl alcohol, if it can be utilised for the production of denaturing wood-spirit.

The use of purely chemical methods for the manufacture of methyl alcohol from crude wood-spirit must be regarded as impracticable. The only practicable method for separating acetone and allyl alcohol from the bulk of the methyl alcohol is fractional distillation.

Acetone boils at 56.3°C. , methyl alcohol at 66.5°C. and allyl alcohol at 97°C.

Acetone and methyl alcohol form a constant-boiling mixture which contains about 90 per cent of acetone and 10 per cent of methyl alcohol. The boiling-point of this mixture is 55.9° and is therefore lower than that of either component. On distilling crude wood-spirit, which contains a larger proportion of methyl alcohol than of acetone, the constant-boiling mixture comes over first, and the bulk of the methyl alcohol, free from acetone, remains in the residual liquor. The constant-boiling mixture is known as *methyl acetone*; it is employed for denaturing purposes and also as a solvent.

The difference between the boiling-points of methyl acetone and methyl alcohol, though not very great, is sufficient to ensure almost quantitative separation of the acetone from the

bulk of the methyl alcohol as long as a sensitive column still is employed, a certain and by no means insignificant proportion of the methyl alcohol coming over, of course, with the acetone. Separation of the remaining components of wood-spirit is a much simpler process. Of these, the aldehydes, amines, ammonia and methyl acetate pass into the "first runnings" with the acetone; on the other hand, allyl alcohol, higher ketones, hydrocarbons and "wood-oils" appear as "last runnings."

In the manufacture of crude wood-spirit from dilute (10 per cent) aqueous solutions or from acetate liquor, the main bulk of the distillate is not collected in separate fractions (see p. 245) as long as the product is intended for immediate disposal; on the other hand, if crude wood-spirit is manufactured with a view to further treatment for pure methyl alcohol, those portions of the distillate which are rich in acetone, and those portions which contain relatively little acetone, must be taken off as separate fractions.

In order to ensure proper division of the distillate, the distiller makes use of a simple method of estimating acetone, which depends on the insolubility of the latter in caustic soda solution with a specific gravity of 1.3. 20 c.c. of the liquid to be tested are introduced into a graduated stoppered cylinder, and 40 c.c. of the caustic soda solution are added; the mixture is shaken vigorously, allowed to stand until it is quite clear, and then cooled to 15° C. The acetone separates out and forms a layer above the caustic soda solution; the volume of the layer in cubic centimetres is read off and multiplied by five; the result represents the number of cubic centimetres of acetone in 100 c.c. of the original liquid. The acetone which separates out in this manner is by no means pure, but contains all other components of the original liquid which are insoluble in caustic soda solution of the above concentration, such as methyl acetate, so far as this product is not saponified, and any acetaldehyde which has escaped resinification; consequently, the value for the acetone content, as determined by the above method, differs very considerably from the value obtained by titration according to Messinger's method (p. 422).

In spite of this fact, the method, which is rapid and can be easily carried out by any workman, serves perfectly well to guide the operator in apportioning the distillate. It gives reliable results until the acetone content of the distillate falls

below 8 per cent. At this concentration separation is no longer clearly visible and it is necessary to make use of a time-reaction for estimating the acetone. This method is based on the length of time which elapses before the precipitation of iodoform, after addition of a mixture of iodine and alkali to the liquid. The formation of iodoform takes place more or less rapidly according to the acetone content of the liquid; by measuring the time required for precipitation it is possible, therefore, after a little practice, to determine the approximate acetone content without difficulty, as long as the tests are performed under equal conditions.

The flow sheet facing p. 258 illustrates the process of manufacture of pure methyl alcohol from dilute aqueous naphtha by *intermittent* fractional distillation.

In carrying out the first distillation of dilute (10 per cent) aqueous naphtha, assuming of course that the latter is not being treated simply for commercial use, it is usual to take off three fractions, namely: (1) the "*first runnings*," which are miscible with water in all proportions, show a concentration of 93 per cent by weight, and at the outset contain 70 per cent of acetone as determined by shaking with caustic soda; this portion of the distillate is collected as one fraction, until the average acetone content of the latter does not exceed 20-25 per cent; (2) the "*middle runnings*," which are also miscible with water in all proportions, show a concentration of about 97 per cent by weight, and contain 1.0-2.5 per cent of acetone; and (3) the "*last runnings*," which show a concentration of about 60 per cent, and are turbid and oily.

In the smaller refineries the fractions are collected in glass receivers or carboys; in the larger establishments the fractions are conveyed directly from the outlet of the condenser into tanks, installed above the boiling-vessels of the stills in which further treatment of the products will be carried out.

The former method of collecting the fractions requires considerably more labour and may easily result in loss, owing to fracture of the vessels or during the operation of transferring the contents by decantation or pumping; at the same time, however, it offers greater certainty in separating the distillate into the proper fractions.

By conveying the liquor directly into tanks, all hand-labour and all the above sources of loss are eliminated; on the other hand, it may easily happen that, owing to carelessness

on the part of the operators, the "first runnings," rich in acetone, find their way into the "middle runnings," weak in acetone.

If tanks are employed, it is essential to exercise proper supervision—at any rate at the outset—and above all to provide a carefully organised system of analytical control.

In starting up a new plant it is usual to begin with the glass vessels, and at a later stage, when the operators have become thoroughly familiar with the process, to change over to the tanks, which are indispensable to the manufacture of methyl alcohol on a large scale.

No matter which of the two methods is adopted, the fraction in each separate container must be sampled, the acetone content determined, and the result carefully recorded. These conditions must be strictly observed, since the manufacture of pure methyl alcohol depends for success on careful supervision and systematic treatment of the various fractions in accordance with the amount of acetone present.

None of the fractions obtained from the first distillation of dilute aqueous wood-spirit represents a finished commercial product.

The "first runnings" tend to become discoloured and are too weak in acetone and allyl alcohol.

The "middle runnings" still contain too much acetone and allyl alcohol to allow of the product being used as "pure" methyl alcohol, say, for the manufacture of formaldehyde; and the "last runnings" are mostly too dilute to be serviceable for any purpose.

As soon as the collecting tank which receives the "first runnings" from the first distillation (I) and corresponding fractions from other stages of the process is full, the contents are analysed and then introduced, by gravitation if possible, into the boiling-vessel of a column still similar to that employed for the first distillation.

Experience has shown that rectification proceeds much more satisfactorily and with the expenditure of a substantially smaller amount of steam, if the concentrated "first runnings," which usually show about 93 per cent by weight, are diluted down to a concentration of 40–50 per cent beforehand.

The dilution is generally carried out in the boiling-vessel of the still itself.

A sufficient quantity of mineral acid is also added in order

to neutralise the amines, ammonia and other bases which are present in the "first runnings"; the addition of acid at this stage also renders the distillate less liable to become discoloured.

The second distillation (II) is then carried out exactly as described for the first.

The first fraction, which contains a relatively large proportion of acetone and corresponds to about 50 per cent of the original charge, is run into the collecting-tanks reserved for *German or Austrian denaturing wood-spirit* (see pp. 428, 431); this fraction, after having been treated with a suitable quantity of "last runnings" containing allyl alcohol, or of acetone oils, and tested analytically, is then ready for shipment.

The second fraction, which already contains less acetone, may be utilised as *English denaturing wood-spirit* (see p. 432) without further treatment, or it may be returned to the process and redistilled with the next batch of "first runnings" from the first distillation.

By this time the acetone content has diminished to such an extent that the next fraction contains only 2 per cent. This fraction is collected in a special tank which is reserved for fractions containing 1-2 per cent of acetone. Finally, a fraction comes over which contains less than 1 per cent of acetone, and which may be allowed to mix with the "middle runnings" (acetone content 1.0-2.5 per cent) from the first distillation. Weak "last runnings," containing allyl alcohol, form the last fraction from the second distillation.

The third distillation (III) is carried out with the "middle runnings" (containing up to 2.5 per cent of acetone) from (I); this product is mixed with fractions containing a similar proportion of acetone from other operations, and again the mixture is diluted before rectification; small quantities of caustic soda solution are also added for the purpose of saponifying any methyl acetate still present, and resinifying aldehydes, etc.

The "first runnings," rich in acetone, from this operation are mixed with the corresponding fraction from the first distillation; the succeeding fraction, which contains 2 per cent of acetone, is run into the tank reserved for fractions of that particular concentration; and the main bulk of the distillate, which contains 0.4 per cent, or less, of acetone, is likewise run into a special container.

last product, on what is now the *fourth distillation* ves, as "middle runnings," "*pure*" methyl alcohol, containing less than 0.1 per cent of acetone.

A fraction is preceded by others containing 2 per cent, or more of acetone; these are run into the corresponding tanks and return to the process.

The weak "last runnings," derived from the separate operation containing allyl alcohol, are likewise collected in one tank in which they are highly diluted with water for the purpose of separating out the wood-oils; the latter are then removed mechanically and the residual aqueous solution is discarded.

The "first runnings" from this operation are added to the process for recovery of methyl alcohol; the residue of the distillate, rich in allyl alcohol, is added to the denaturing wood-spirit, as far as the official specifications permit.

Hence, one of the main principles of this process is the systematic distribution of the various fractions, according to their acetone content, among a series of tanks each of which is reserved for liquor containing a certain definite percentage of acetone.

Each separate distillation, apart from the first, furnishes, on the one hand, *marketable products* (denaturing wood-spirit; "pure" methyl alcohol, for formaldehyde manufacture; "pure" methyl alcohol, containing 0.03-0.05 per cent of acetone, for the aniline-dye industry; "pure" methyl alcohol, containing 0.01 per cent of acetone, for the preparation of perfumes), and on the other hand, *intermediate products* which must be submitted to further rectification, until step by step the final objective—pure methyl alcohol—is reached.

Manufacture of pure methyl alcohol from wood-spirit by *intermittent* fractional distillation is a lengthy process which obviously cannot lead to successful results without the exercise of close analytical control.

Repeated distillation gives rise, unavoidably, to loss of material; the necessity of repeatedly boiling up dilute solutions of wood-spirit involves the expenditure of large amounts of steam and cooling water; and the capital cost of the installation is high, since the plant comprises several large column stills which together with their equipment are constructed entirely of copper, and naturally occupy a considerable amount of space. In view of these facts it is not surprising

that other methods for the rectification of crude wood-spirit have long been sought after.

Here again, the introduction of a process of *continuous* distillation has brought about considerable changes in recent years.

We have seen above that it is possible, by a single continuous process of distillation, to isolate wood-spirit in concentrated form from aqueous solutions of calcium acetate in which it is present to the extent of only 3 per cent, and in addition to effect the continuous separation of the products otherwise contained in the "last runnings," namely the "wood-oils."

An apparatus of this type separates wood-spirit and wood-oils from the water accompanying those products; towards the latter water acts as "last runnings," and consequently collects at the bottom of the lower column. Further, the apparatus separates wood-oils from wood-spirit, since the former act as "last runnings" in relation to the latter, and therefore collect in the lower portions of the upper column, from which region they are removed. The wood-spirit behaves as "first runnings" towards the water and the wood-oils, and therefore will be found at the top of the column still.

Moreover, since the acetone, aldehyde, methyl acetate and other products contained in the first fractions act as "first runnings" in relation to the methyl alcohol, it will be obvious that, given a suitable combination of several continuously operating columns working in conjunction with one another, it should be possible to isolate methyl alcohol continuously from crude wood-spirit in one single operation, and without the necessity for analytical control which in the intermittent process occupies practically the whole time of one chemist.

Continuous rectification of a crude product to a fine product with simultaneous recovery of the by-products is not a new idea, for the spirit industry, after many fruitless attempts, solved it long ago, and nowadays large quantities of fine spirit are manufactured in continuous stills directly from the mash itself. The intermittent column stills used in the wood-distillation and other industries were evolved from the apparatus used in the spirit industry, and similarly the first attempts to manufacture pure methyl alcohol from crude wood-spirit in one operation were made with the continuous plant used in the spirit industry—but with negative results.

The manufacturers of this type of apparatus were not yet in

a position to render it suitable for the production of pure methyl alcohol.

Before success was achieved much alteration of the apparatus was necessary, as well as years of experimenting by the actual wood-distillers themselves, who were better acquainted than the manufacturers of the plant with the behaviour of wood-naphtha on fractional distillation.

To-day the problem must be looked upon as solved beyond any doubt.

In carrying out the process of continuous rectification of *crude wood-spirit* for the manufacture of pure methyl alcohol and denaturing spirit, the crude product is first of all diluted in a tank; the dilute liquor is then run into the lower portion of a column still—the boiling column—and heated by direct steam. In this section of the plant the wood-spirit is only separated from the water, and deprived of esters and of any bases which may be present. The vapours of wood-spirit enter the second column, where the usual process of condensation and re-vaporisation takes place, the plates of the column becoming covered with liquids possessing different boiling points.

The lower plates contain the higher-boiling components, the liquid in this case consisting of a mixture of methyl alcohol, water, allyl alcohol and wood-oils; the upper plates contain the more volatile components, in particular a mixture of acetaldehyde, acetone, methyl acetate, methyl alcohol and water. The middle section of this column—the first rectifying column—naturally contains the “*middle runnings*” already freed from the main bulk of the “*last*” and “*first runnings*”—in other words, methyl alcohol already very weak in acetone.

It will be obvious that if crude wood-spirit is supplied continuously to the first column and the three products are not continuously removed from the second column, these zones will eventually overlap. The second column is therefore provided with three separate condensers:

1. A *lower condenser*, which condenses the “*last runnings*” and removes them from the process.
2. A *middle condenser*, which condenses the “*middle runnings*” and delivers them to a third column—the second rectifying column—for further treatment.
3. An *upper condenser*, which condenses the “*first runnings*” (denaturing wood-spirit) and removes them from the process.

It will also be clear that in any given unit of time the sum of the wood-spirit components which are condensed and separated by means of these condensers must not exceed the total quantity of wood-spirit entering the first column.

The condensed denaturing wood-spirit only requires suitable admixture, either with "last runnings" which have been concentrated by a special intermittent distillation, or with acetone oils, to render it ready for shipment.

The "*middle runnings*," already containing only a small proportion of acetone, are introduced into a second rectifying column, and heated by steam; more acetone is removed and the distillate rich in acetone is passed into the acetone zone of the first rectifying column. The methyl alcohol, which is now almost entirely free from acetone, but is dilute as a result of the introduction of live steam, passes into a second boiling column. In the latter exactly the same process takes place as in the first boiling column; but in this case the feed-liquor consists of almost pure methyl alcohol, still contaminated, however, with traces of "first runnings" (acetone) and "last runnings" (allyl alcohol, wood-oils), whereas the feed-liquor to the first boiling column consisted of very impure methyl alcohol, namely, crude wood-spirit.

The sole function of the second boiling column is to deliver the three components acetone, methyl alcohol and allyl alcohol, together with a corresponding quantity of water, *all in the form of vapour*, to a third rectifying column. The formation of zones, of which the respective heights in the column are inversely proportional to the boiling-points of the products, can only take place if the mixture is supplied in that form.

The third rectifying column separates the inflowing vapours in such a manner that the water condenses on the lowest plates; it still contains a certain amount of methyl alcohol, however, and is therefore run back again to the boiling column. The "*last runnings*" collect in a zone immediately above the water and are removed from this region. The *finished methyl alcohol*, practically free from acetone and conforming to all other tests, is taken off as "*middle runnings*" from the upper plates, and from the top plates of all, small quantities of acetone which still remain are run into the acetone zones of the preceding columns.

In this way the crude wood-spirit which flows continuously

into the first boiling column is completely resolved, during its passage through the four succeeding columns, into—

Denaturing wood-spirit.

“ Last runnings.”

Pure methyl alcohol, containing only 0.03-0.10 per cent of acetone.

The series of operations described above can be modified of course, and rendered more simple, but even then, the management of an apparatus in which the alteration of a single factor immediately affects every part of the plant will scarcely be regarded at first sight as a particularly easy or pleasant duty.

Until the operators have become thoroughly familiar with the operation of the plant, the above view is justified, especially for apparatus of moderate dimensions. Later, however, no difficulties are experienced either in starting up the plant or in keeping it in normal operation.

Certain conditions are indispensable for the normal operation of a continuous column still, namely: uniform supply of crude wood-spirit which must also be of uniform composition; maintenance of uniform steam pressure in the boiler; the use of sensitive steam-regulators for the columns which are heated by direct steam; maintenance of a constant head of cooling water which should be supplied at a uniform temperature and should be as soft as possible.

Compared with the intermittent column still, the advantages of the continuous apparatus consist in the small number of operators necessary, small consumption of steam and cooling water, smaller losses, the small amount of space occupied, and very efficient separation of the product in a high state of purity. These advantages, however, are only realised if the output is moderately large.

Even if the output is small, the continuous process may be recommended for the *first* rectification of crude wood-spirit, since “ middle runnings ” obtained in this way are already sufficiently free from acetone to be capable of giving pure methyl alcohol directly, as the result of one subsequent distillation by the intermittent process.

In regard to the *yields* of the different products obtainable by the above processes, it is impossible to give figures which hold good generally, since the yields depend entirely on the quality of the crude wood-spirit, and more especially on the proportions of acetone and wood-oils present.

When the price of denaturing wood-spirit is high, the manufacturer will keep the acetone content down to the lowest permissible figure in order to be in a position to sell the largest possible quantity of the product. In these conditions it follows that the yield of pure methyl alcohol must be correspondingly low.

In opposite conditions the manufacturer will endeavour to bring up the acetone content of the denaturing spirit to the highest permissible figure, in order to leave as little methyl alcohol as possible in the product. As a result the yield of pure methyl alcohol will be increased.

In general it is safe to reckon that the treatment of crude wood-spirit for denaturing spirit and pure methyl alcohol will result in a loss of 5-10 per cent per 100 kilos. of wood-spirit (100 per cent). The extent of the loss depends on the proportions of wood-oils, amines, ammonia, aldehydes, etc., present in the raw material, since these components either give rise to valueless products or are destroyed.

We have seen above that crude wood-spirit possesses the following approximate composition :—

	Per cent.
Acetone	13·0
Methyl alcohol	52·5
Aldehyde, methyl acetate, allyl alcohol, ketones, etc.	7·5
Water	27·0

Assuming a loss of 10 per cent, and the production of denaturing wood-spirit containing 25 per cent of acetone, the following yields should be obtained from 100 kilos. of the crude wood-spirit :—

	Kilos.
Denaturing wood-spirit	47
Pure methyl alcohol	19

Or from 100 kilos. of crude wood-spirit at 100 per cent :—

	Kilos.
Denaturing wood-spirit	64
Pure methyl alcohol	26

On the other hand, if the acetone content of denaturing wood-spirit is increased, for example, up to 40 per cent, the ratio of yields becomes entirely different—a fact which demonstrates the impossibility of stating figures which will apply universally.

III. RECOVERY OF ACETATE OF LIME FROM AQUEOUS SOLUTION

The concentration of the acetate liquor varies according to the particular process which is employed for the removal of tar from pyroligneous acid, and the particular manner in which the distilled pyroligneous acid is neutralised with milk of lime. The acetate liquor obtained from hardwood pyroligneous acid by the A, C and D processes (pp. 200, 211, 219) contains 10–12 per cent, and by the B process (p. 204) 25 per cent of anhydrous calcium acetate.

The solubility of calcium acetate in hot and cold water does not differ very greatly;¹ consequently recovery of the product by a process of evaporation and crystallisation is impracticable.

It is necessary, therefore, to employ a method similar to that adopted for the recovery of common salt from brine; in other words, the solution instead of being evaporated to the crystallising point must be evaporated to dryness.

The solubility limit of grey acetate of lime is reached when the hot solution contains about 40 per cent of the dry salt. If this concentration is exceeded crystals of calcium acetate at once begin to separate out—similar to the case of common salt—and after only slightly further concentration, the solution sets to a crystal-paste which, in thick layers, cannot possibly be dried completely. By centrifuging this paste, which contains rather more than 40 per cent of grey acetate of lime, attempts have been made to concentrate it still further, but owing to the small difference in the solubility of acetate of lime in cold and hot water, the liquor expelled during the process contains only little less acetate than the crystal-magma remaining in the centrifuge; consequently, the centrifuging process, which in view of the amount of power consumed is not exactly cheap to run, proves more or less useless, or at any rate does not offer advantages in proportion to the charges entailed for labour, depreciation and power.

The only feasible method of producing finished grey acetate of lime (80 per cent) from the crystal-paste consists in drying the latter by the application of heat.

With this object, the paste is spread out in comparatively

¹ Actually, between 0° and 100° C., calcium acetate is more soluble at lower than at higher temperatures. Cf. *Lumsden*, Journ. Chem. Soc., 1902, **81**, 355.

thin layers on heated surfaces, and turned over repeatedly with a shovel until it is perfectly dry ; this state is indicated when small pieces, on being crushed between the fingers, immediately fall into powder. The process consists, therefore, in *kiln-drying* the crystal-paste.

Formerly it was believed that this process, at any rate in its final stages, must be carried out at a really high temperature, in order to provide for the vaporisation of empyreumatic matter present in the acetate.

It has already been stated that acetate of lime contains absolutely no free volatile " empyreumatic " matter, and that the organic impurities must be regarded chiefly as aldehyde-resins combined with lime, which have resulted by the action of lime, or possibly calcium acetate, on the aldehydes present in pyroligneous acid, during the process of neutralisation and the subsequent operations for recovering naphtha.

In addition, the acetate of lime contains certain amounts of phenols likewise combined with lime. None of these products, however, can be removed by heating the acetate, at any rate not without bringing about simultaneous partial decomposition of acetate into acetone and calcium carbonate, thus giving rise to loss.

When acetate of lime is heated to 150° C. loss of volatile matter can already be detected, probably owing to the formation of ketones from the homologous calcium salts of propionic and butyric acids present in the acetate.

In order to avoid loss of valuable material the drying process must be carried to completion at a temperature—measured in the dry material—not exceeding 125–130° C.

The final stage of drying, therefore, is not in any sense a *roasting process* for the purpose of expelling volatile organic matter, as was formerly assumed and is often assumed even at the present day. It is solely a *drying process* which is carried out at a comparatively low temperature with the object of removing so much moisture by evaporation that only 8–10 per cent remains in the residual mass.

If any attempt be made to reduce the moisture content still further, by raising the temperature of drying, then ketone formation sets in with resulting loss.

Another characteristic of solutions of acetate of lime is that on evaporation tarry or possibly resin-like masses form on the surface of the liquor ; the quantity of these products is not very

large, but it is found that if they are removed by skimming during the process of evaporation the quality of the finished acetate is improved. These products are mostly formed during the actual process of boiling down the liquor, possibly owing to phenolic bodies, such as pyrocatechol, becoming liberated from their calcium compounds by the action of atmospheric carbon dioxide, and then undergoing resinification by atmospheric oxygen in the presence of free caustic lime or even calcium acetate. A further possibility is that, owing to the presence of aldehydes or other substances exhibiting similar behaviour, aldehyde-resins are formed at the boiling-temperature of the liquor as a result of the prolonged action of lime or calcium acetate.

In every case, so far as the process permits, these masses of tarry and resinous matter should be removed; as a result the content of acetate in the final product will probably be increased.

We have now to consider the methods employed in practice for evaporating the acetate liquor and drying the solid product.

In the first place the acetate liquor, no matter by what process it has been obtained, must be evaporated down to the consistency of a paste, which will contain about 60 per cent of water and 40 per cent of grey acetate (80 per cent acetate of lime).

At one time this process was largely carried out in cast-iron or steel pans heated by direct fire.

The acetate liquor always contains a certain amount of free lime and even calcium carbonate in solution. As concentration proceeds, these impurities separate out, forming a rather firm scale which becomes baked hard on to the bottom of the pan, thus rendering transmission of heat much more difficult. In these conditions a uniform rate of evaporation can only be maintained by increasing the temperature of the furnace gases heating the pan, since the amount of heat transferred is proportional to the temperature difference and the coefficient of transmission. If the latter decreases, it follows that the temperature difference, and therefore the temperature of the furnace gases, must be increased, if the rate of evaporation is to remain constant.

As a result, however, it may easily happen that the scale, with which more or less acetate of lime is always intermingled, becomes overheated, and decomposition of the acetate into

acetone and calcium carbonate may then set in, thus causing loss.

Nowadays, direct-fired pans are only found in small, primitively equipped establishments; but the American and Canadian factories still largely employ pans of the same type, heated by means of the less dangerous flue gases from the retort furnaces, the temperature of which can scarcely exceed 400°C .

The pans employed in these cases are mostly constructed of steel, in the form of shallow rectangular boxes.

The coefficient of transmission of heat between liquids and furnace gases is low, amounting in the case of acetate liquor, which readily forms scale, to not more than 15 kilo-calories

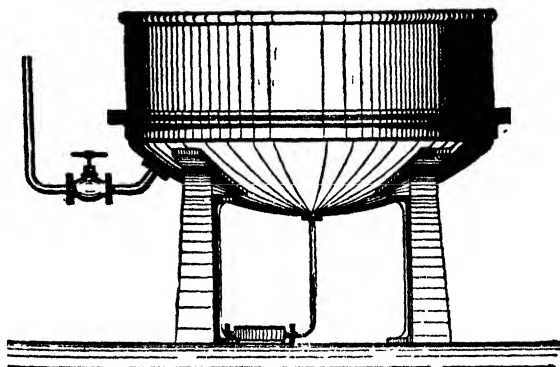


FIG. 35.—CIRCULAR OPEN COPPER PAN FOR EVAPORATING ACETATE LIQUOR.

(that is, for every 1 sq. m. and 1°C . temperature difference 15 kilo-calories pass from the furnace gases into the acetate liquor per hour); moreover, the temperature difference between the boiling acetate liquor and the flue gases, which enter at a maximum temperature of 400°C . and should leave at 300°C . (to avoid difficulties with the chimney draught), is comparatively small. In these conditions it is only possible to transmit $250 \times 15 = 3750$ kilo-calories or to evaporate $\frac{3750}{530} = \text{approx. } 7$ kilos. of water per 1 sq. m. of pan surface, compared with at least 30–35 kilos. for pans heated by high-pressure steam.

It is obvious, therefore, that pans heated by direct fire or furnace gases cannot be regarded as modern forms of evaporating plant, especially for this particular purpose.

The apparatus most frequently employed for the evaporation of acetate liquor is shown in Fig. 35. It consists of a cylindrical copper vessel 2 metres in diameter, with a dished copper bottom which is surrounded by an outer jacket of steel. The steam used for heating the pan is passed into the annular space formed by this double bottom. Stay bolts are usually fitted between the bottom of the vessel and the outer steel jacket, so as to afford greater resistance to the pressure of the steam, which amounts to 3-4 atm. A steam valve, safety valve and steam trap complete the equipment of a pan of this type.

It is usual to employ *copper* for the construction of these pans, because the scale which forms on the heating surface can be removed much more easily from copper than from iron. Moreover, the acetate produced from liquor which has been evaporated in a copper pan is lighter in colour than that from an iron pan.

The American and Canadian factories use jacketed pans made entirely of steel, and of the shallow box form shown in Fig. 36.

Whatever the particular advantages possessed by the one or other form of pan, it is obvious that the steel pan must be considerably cheaper than the cylindrical pan which is constructed mostly of copper.

Small factories will probably feel more inclined to the copper pan, larger factories to the box form.

The concentration of anhydrous calcium acetate in the acetate liquor varies from 12 to 25 per cent, according to the method employed for removing dissolved tar from the pyro-ligneous acid.

Liquor with a concentration of 25 per cent is usually evaporated directly to a paste: 12 per cent solutions, and more particularly solutions containing under 12 per cent, are treated in special closed evaporators heated by waste steam. These evaporators permit repeated utilisation of the latent heat contained in the water vapour which escapes during evaporation, thus bringing about considerable economy in steam consumption.

In these evaporators the weak acetate solutions are concentrated to the highest permissible degree before treat-

ment in the open evaporating pans (old system) or on the rotating "drum-driers" (new system).

The behaviour of the acetate liquor has already been described above, and it has been mentioned that when the dry salt concentration of the hot solution reaches 40 per cent, separation of acetate of lime in clusters of crystals readily takes place.

Hence, closed evaporators can only be employed to evaporate

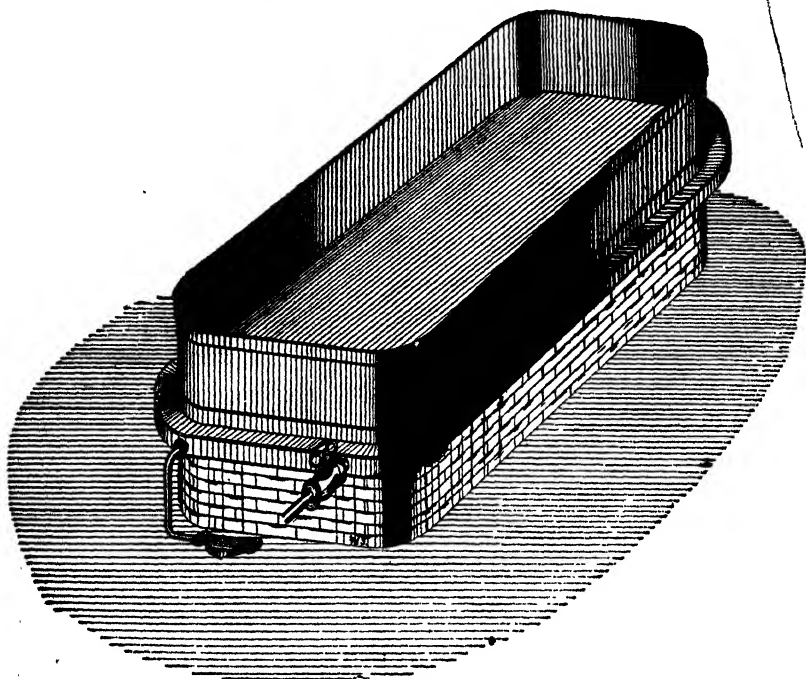


FIG. 36.—SHALLOW OPEN STEEL PAN FOR EVAPORATING ACETATE LIQUOR.

the weak acetate liquor to a concentration not exceeding 35 per cent of grey acetate of lime.

The evaporation of acetate liquor in a closed apparatus which permitted repeated utilisation of latent heat was first introduced into the wood-distillation industry by the author.¹

The principle of this apparatus consists in dividing the acetate liquor into two or more portions which are distributed

¹ German patent 193,382.

among the same number of separate vessels or effects (see also p. 212).

These vessels are usually constructed in the form of cylinders, composed of steel. The lower portion of each vessel contains a heating system (see Fig. 37) built up of heating tubes which extend between two tube-plates. The liquor undergoing evaporation fills the pan forming the bottom of the vessel, the tubes, and a certain amount of the space in the portion of the vessel above the upper tube-plate; the heating agent (live steam, exhaust steam, hot gases) circulates round the tubes. Transference of heat to the solution can only take place if a certain difference in temperature exists between the heating agent and the solution.

When steam is used as the heating agent, this difference is always created by keeping the pressure inside the apparatus either above or below the external pressure.

For example, suppose that an attempt were made to utilise exhaust steam with a minimum temperature of about 100°C . for evaporating acetate liquor, which during concentration evolves steam at the same temperature, it would be found impossible to effect evaporation unless the pressure inside the evaporator were *reduced* to a certain definite extent. By reducing the pressure it is possible to lower the boiling-point of the acetate liquor far enough to ensure that a sufficient difference in temperature exists between steam and liquor; the acetate liquor can then be evaporated almost free of cost, since the creation of reduced pressure by means of a vacuum-pump requires only a small amount of power and therefore of steam.

In order to create the necessary reduction of pressure inside the apparatus, which in simplest practice consists of only one vessel, the dome of the vessel is connected with a so-called "wet vacuum-pump"; this pump effects the condensation of the water vapour escaping from the evaporator by spraying it with cold water in a separate chamber. At the same time it discharges the condensed liquid and expels a certain amount of air which always comes over with the water vapour.

An apparatus of this type permits the fullest utilisation of waste steam, and thus constitutes a steam economiser of the very first rank for all factories in which a certain amount of waste steam is available and is not otherwise employed; for

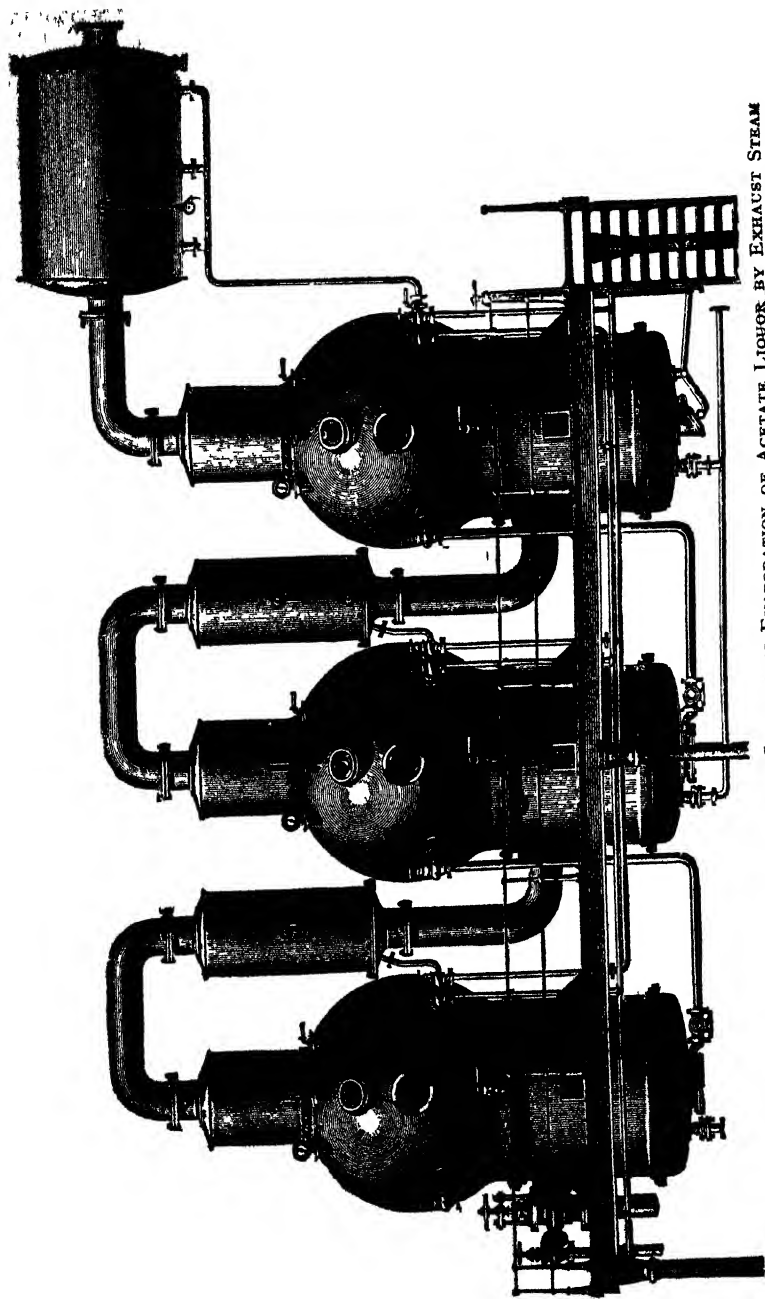


FIG. 37.—MULTIPLE EVAPORATOR¹ FOR THE CONTINUOUS EVAPORATION OF ACETATE LIQUOR BY EXHAUST STEAM OR OTHER SOURCES OF WASTE HEAT.

¹ German patent 193,382.

example, factories in which wood-distillation plants are worked in combination with blast furnaces or with plant for the manufacture of acetic acid, etc.

When larger evaporators are employed it is usual to provide separate surface condensers, or possibly jet condensers, and a slide-valve air pump instead of a wet vacuum pump.

The surface condensers act in the ordinary manner, that is, heat exchange takes place between the vapours and the cooling water, through the medium of a metal partition. In the jet condensers, however, the heat exchange takes place directly between the water vapour and the cooling water; the vapour flows into a cylinder in which it is brought into contact in some suitable manner with an opposing spray of cooling water.

When an apparatus operating under reduced pressure is employed, the condensed liquid produced by one or other form of condenser must be removed by means of interchangeable receivers, by a special pump, or best of all by arranging that the condenser outlet is situated about 10-11 metres above the floor, and delivers the cold distillate into a long pipe which dips into a tank full of water standing on the floor. The air pump is connected with the condenser by means of a branch pipe at the outlet, or at the top of the jet condenser if the latter form is used, and removes air continuously from the apparatus.

In this way it is possible, even under the reduced pressure which is created as a result of condensation and the action of the air pump, to discharge the condensed liquid continuously through the barometric pipe connecting the condenser outlet with the water seal on the floor below.

Suppose that the steam escaping from the vessel containing the acetate liquor, instead of being condensed by one of the methods described above, is caused to circulate round the heating tubes of a second vessel, inside which the pressure is still lower than in the first vessel. In these conditions the boiling-point of the liquor in the second vessel will also be lower and it will be possible, by utilising the steam escaping from the first vessel, to evaporate a second portion of acetate liquor almost equal in quantity to the first. An apparatus of this kind is known as a "double effect." In this case the interior of the first vessel is connected with the condenser and air-pump through the heating system of the second vessel,

whereas the interior of the second vessel communicates directly with the pump.

The course of the process is then approximately as follows :—

The first and second vessels are filled with the dilute acetate liquor. The first vessel is heated with waste steam at 100°C . The valves are adjusted in such a manner that a "vacuum" of about 40 cm. of mercury (36 cm. pressure), corresponding to an internal temperature of about 80°C ., is created inside the vessel. The steam evolved at 80°C . from the first vessel enters the heating system of the second vessel, in which a "vacuum" of about 64 cm. of mercury (12 cm. pressure) is maintained; under this pressure the liquor in the vessel boils at about 55°C . The steam escaping from the second vessel passes into the condenser or is used for heating a third vessel; in the latter case the evaporator is known as a "triple effect," and if a fourth vessel is employed, as a "quadruple effect."

In the above example, a difference in temperature between the heating agent and the solution, amounting to $20\text{--}25^{\circ}\text{C}$., is created in each vessel by reducing the pressure to a different extent in each case.

Hence, by introducing one and the same quantity of steam into the heating system of the first vessel it is possible to evaporate a certain quantity, or double or treble that quantity, of acetate liquor, according to whether a single, double or triple effect is employed; in other words, it is possible, theoretically, to reduce the quantity of steam required to evaporate the liquor in open pans to one-half or one-third, and therefore to effect a saving of 50–66 per cent in steam consumption.

In actual practice the figures are not so favourable, but at the same time the differences are not very great. It is always an advantage, therefore, to employ vacuum evaporators if a sufficient quantity of waste steam is available. If this quantity exceeds that required for evaporating a certain definite amount of acetate liquor, a single effect is used; if only about 60 per cent of the required quantity is available then a double effect must be employed; if only 40 per cent, then a triple effect is necessary, in order to bring about full utilisation of the waste steam, and at the same time to effect maximum economy (100 per cent) in the consumption of steam for evaporation of acetate liquor.

If no waste steam is available the first vessel must be heated with high-pressure steam ; in these conditions economy in steam consumption can only be effected if a double or a triple effect is employed and the process is carried out exactly as described above for the use of waste steam.

In this case the saving in steam compared with evaporation in open pans amounts to about 40 per cent for the double effect and about 60 per cent for the triple effect.

Since acetate solutions in general are capable of enduring high steam temperatures without undergoing any injury, it is also possible to use evaporators in which the differences in temperature are attained by applying excess pressure varying in degree, instead of reducing the pressure.

Thus, in the first vessel an internal pressure of 3.5 atm. (temp. = 139° C.) may be maintained ; in the second, 2 atm. (temp. = 120° C.) ; and in the third, atmospheric pressure (temp. = 100° C.).

Steam, introduced at a pressure of about 6 atm. (temp. = 159° C.) into the heating system of the first vessel, evaporates the acetate liquor contained in that vessel under a pressure of 3.5 atm., and steam at 139° C. is evolved. The latter evaporates the liquor contained in the second vessel, and steam at 120° C. is evolved, and is capable in turn of evaporating the liquor under atmospheric pressure in the last vessel.

In certain respects these pressure evaporators are simpler than the vacuum type ; no air pump is required, and the condensed-water pumps which form part of the equipment of a vacuum evaporator are also omitted. (The function of these pumps is continuously to remove the condensed water which collects in the heating systems of the second and third vessels, both of these heating systems being under reduced pressure.)

In plant operating under excess pressure this function is performed by simply constructed condensed-water drainers.

Pressure evaporators, especially the heating systems, must naturally be of stouter construction than vacuum evaporators ; accordingly, the capital cost is higher.

As a general rule, pressure evaporators are only employed where no waste steam is available.

In wood-distillation factories mechanical power is always needed for supplying condenser water, for generating electric light, for driving agitators, fans, etc. ; hence, there is usually

a sufficient quantity of waste steam available for preconcentrating acetate liquor up to 30–35 per cent at least in multiple vacuum evaporators.

It has already been mentioned above that the plant in which the *preliminary* evaporation is carried out might also be heated by means of hot gases (furnace gases, gaseous products from the carbonising apparatus); in fact, as long as the acetate liquor remains completely liquid, it is a matter of indifference whether gases or steam are used for the purpose.

If a sufficient quantity of gas is available, and as long as the chimney draught will not suffer if this gas is cooled down, it is quite feasible to employ it for heating open or closed evaporators in preconcentrating the acetate liquor.

With multiple evaporators, for example, it is only necessary to heat the first vessel with furnace gases. Evaporation inside the vessel is allowed to take place under a certain excess pressure, and in this way steam at a temperature sufficient to effect evaporation in the second and even in a third vessel is obtained, the internal pressure in the vessels diminishing step by step from the first vessel to the last.

The adoption of this system of heating entails not only considerable modifications in the arrangement of the furnaces, but also the provision of much larger heating surfaces than are required by evaporators heated by high-pressure or waste steam, owing to the fact that the coefficient of transmission of heat between *gases* and solutions is much smaller.

Moreover, when gas, instead of steam, is used as the heating agent, the regulation of the apparatus—especially a multiple evaporator—is naturally much more difficult; for these reasons a gas-heated evaporator is only employed in quite special circumstances.

We have now to consider the next operation which consists in further evaporation of the preconcentrated liquor until it has acquired the consistency of a thick paste. This operation is carried out in open vessels which permit removal of the paste without difficulty.

The liquor from the evaporators passes first of all into iron settling tanks; the clear liquor, usually still hot from the preceding operation, is run from the tanks into the open evaporating pans described above (Figs. 35, 36; pp. 268, 270); high-pressure steam is then supplied to the pan at a suitable

rate and evaporation soon begins. Either the full charge is introduced at once into the pan, or else only a portion, the remainder being allowed to flow in continuously afterwards.

Each pan is capable of producing a definite quantity of acetate of lime paste, according to the area of heating surface available.

Hence, only a certain definite quantity of acetate liquor, corresponding to the heating surface, may be supplied to the pan. As soon as this quantity is reached the process of replenishing the liquor in the pan must cease, and the operation of reducing the liquor to the consistency of paste may then be completed.

At first, evaporation proceeds very smoothly. It is only necessary carefully to regulate the supply of steam so as to avoid too violent ebullition, as this may easily result in the liquid frothing over; in addition the resin-like masses which separate out must be skimmed off from time to time; otherwise, the process requires scarcely any supervision during this period. As the concentration of the liquid increases, the rate of evaporation diminishes; still further reduction occurs as soon as solid acetate of lime begins to separate out. The solid product settles on the bottom of the pan and interferes more or less with the transfer of heat to the liquor. The operator can still remove this obstruction by stirring the liquor, but the separation of solid acetate increases rapidly, and the whole liquor appears to be interspersed with crystals; finally, a thick stiff paste results, which renders any kind of stirring, even with mechanical stirrers, ineffectual.

Usually the pans are left to themselves before this period sets in.

There can be no question that, during the period when the paste is forming, the consumption of steam is enormously high, and the rate of evaporation is very low in proportion to the heating surface available and the amount of steam used.

It would appear almost impossible for steam to penetrate the layer of paste 300-400 mm. thick, but the eruptions which occur on the surface indicate that evaporation is still going on in the lower portions of the mass, giving rise to bubbles of steam which escape upwards and form small craters at the upper surface of the crystal-paste.

Gradually, these external indications of formation of steam also disappear, and the mass has now been dried as completely

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as the conditions will allow, but the product seldom contains more than 40 per cent of solid substance.

The paste is now shovelled out, and is usually thrown on to a sloping surface to drain. This operation, however, is scarcely worth while, since the yield of drain-liquor is only small.

While the paste is still in the pans, in which it is enveloped in steam and more or less excluded from the air, it usually possesses a brownish yellow colour; but as soon as it is removed from the pans and comes into contact with air, oxidation sets in, and externally the mass assumes a dark brown, dark green or possibly a brownish black or greenish black colouration, according to the proportion of oxidisable matter present; on the other hand, the core of each individual lump remains brownish yellow.

The main bulk of the acetate paste can be removed from the pan without difficulty.

Here again, however, we are faced with the difficulty referred to above in connection with pans heated by direct fire, for each time a batch of liquor is evaporated, the heating surface becomes coated with a very hard crust—often 1 cm. thick—which consists of calcium acetate mixed with calcium carbonate and lime. Since this crust or scale seriously interferes with the efficiency of the pan, it must be removed by means of suitably shaped chisels or scrapers before a fresh batch of liquor is introduced. This operation involves much waste of time, and may easily cause damage to the inner copper bottom of the pan.

Apart from the difficulties which arise from the formation of scale, the latter constitutes an extremely inconvenient by-product, since it is by no means easily dried, and during the process it becomes so hard that it must be broken up in some way or other before it can be used for the manufacture of acetone and especially acetic acid.

The next operation consists in spreading out the acetate paste and scale in thin layers on heated surfaces, in order to complete the process of drying; in other words, both products must be kiln-dried.

In factories which employ horizontal retorts it is usual to construct drying floors over the retorts by covering the top of the retort settings with iron plates or with a special form of tile, below which the flue gases derived from the retort

furnaces are conducted backwards and forwards before entering the chimney.

If the form of carbonising apparatus employed requires that the top of the setting must remain free, the general practice is to construct drying floors of the above type at the ground level, and to conduct flue gases beneath the floors on their way to the chimney.

Frequently it happens that the flue gases are insufficient for the drying process, or the situation of the furnaces is such that a drying-floor cannot be erected in the immediate vicinity.

In these conditions the only alternative is to provide a drying floor heated by direct fire.

In operating a direct-fired floor, arrangements must be made to conduct the furnace gases under the floor in the *same* direction as the acetate paste is travelling on the upper surface of the floor—that is, the hottest portion of the gas transfers heat to the wettest portion of the paste. In this case the adoption of the counter-current principle—so frequently applied when flue gases are used for drying purposes—would involve the danger of decomposition and therefore more or less serious loss of acetate.

When flue gases are used for heating the drying floors, any danger of decomposition or “burning” is practically absent, since the temperature of the gases, by the time they have reached the floor, seldom exceeds $300\text{--}350^{\circ}\text{C.}$, and the acetate paste is exposed to the cooling effect of the air; in these conditions it would be difficult for the temperature of the paste to rise to the decomposition point. On the other hand, when direct-fired drying floors are employed, we have to reckon with an initial temperature—behind the fire-bridge—of $800\text{--}900^{\circ}\text{C.}$ which may easily give rise to local overheating of the acetate.

By employing the like-current principle and providing a suitable brick lining below the plates, even this drawback to the use of direct-fired drying floors can be removed.

The drying floor must be housed in some form of building which will offer suitable protection against the weather; and—as for all drying processes—the building must be properly ventilated.

In order to avoid unnecessary transport of the paste, it is usual to instal the evaporating pans immediately adjacent to

the drying floors ; the paste can then be thrown directly from the pans on to the floors.

The work on a drying floor consists in turning over the material systematically with a shovel.

At first the mass is comparatively wet, and in this condition is easily turned over. As drying proceeds, the material becomes more and more sticky, and then gradually becomes loose again. Finally it forms a rather dusty, crumbly, granular mass—the finished grey acetate of lime.

Each of the above stages—from wet paste to finished product—is characterised by the particular colour of the mass.

At first, the colour of the product is brown to brownish black ; as drying proceeds it becomes continually lighter, until at the end it is grey, yellowish grey, or possibly greyish brown.

The appearance of the product, however, is not always a safe indication of the acetate content. Certain qualities of acetate, for example those obtained from softwood, possess a very light yellowish grey colour, but contain only 73–76 per cent of acetate.

The process of drying acetate of lime by turning it over on a drying floor is by no means easy or agreeable. The workmen's feet suffer as a result of contact with the hot plates, and their eyes and respiratory organs are attacked by the dust and steam. The high temperature of the building also has an injurious effect, and the dust finds its way into neighbouring areas where it may become a serious nuisance. A further disadvantage is the dependence of the process on the state of the weather.

The efficiency of these drying floors depends very largely on the moisture content and movement of the atmosphere ; hence their performance in summer and winter, and on clear sunny days and damp cloudy days, is entirely different.

In view of these facts it is usual to lay down very large drying floors which even in unfavourable weather are still capable of drying the day's output. Such floors, however, occupy a large amount of space ; and a relatively large amount of capital, which at times lies completely idle, is locked up in the iron plates.

As mentioned above, the drying floors are often laid down on top of the retort settings ; as a result, the acetate may easily become contaminated with floating particles of wood,

smuts from the furnaces, etc. Moreover, there is always the danger of the material taking fire if it is not turned over often enough.

In short, no other part of the wood-distillation process gives rise to so many complaints as the operation of drying acetate of lime on the drying floors.

In spite of its disadvantages, this crude process of drying is still in use in the majority of wood-distillation factories, the reason being that mechanically operated drying plant, capable of converting acetate liquor into the dry product continuously and at a sufficiently cheap rate, has not been obtainable at a reasonable price until comparatively recently.

It is true that for many other products plant of the above type has been available for a comparatively long period; mechanical drying of acetate of lime, however, offers very considerable difficulty. If attempts are made to dry the material in rotary apparatus or in apparatus fitted with agitators, through which furnace gases or hot air are passed, it is found that the product, on reaching a concentration of about 50 per cent, becomes converted into a tough, putty-like mass owing to the unavoidable kneading which it undergoes in moving through the apparatus. This mass agglomerates into large lumps which bring any form of agitator or stirring apparatus to a standstill: heat cannot penetrate these lumps, and it is impossible, therefore, to dry them.

Apparatus of this type (rotary cylinders fitted with shelves, stationary cylinders fitted with spiral conveyors, or similar devices for agitating and moving the material) can only be employed to deal with wet acetate of lime which contains 50-55 per cent of the dry product and has been brought up to this concentration in some other form of plant without undergoing any kneading.

Other types of plant, for example the so-called "*belt-driers*," are capable of drying wet acetate of lime containing only 40-45 per cent of the dry product.

These belt-driers consist of a number of horizontally superimposed, endless belts, which are made of metal webbing or metal straps and run over rollers. The system is so arranged that the end of any one belt always projects beyond the end of the belt lying immediately above it. The belts move in opposite directions; the product falls from one belt to the next lower, and in this way is conveyed backwards and forwards, thus

following a zigzag path from the top to the bottom of the system.

The belt system is contained in a closed chamber inside which furnace gases—or preferably hot air since it is cleaner—are conducted over the acetate on the counter-current principle, the belts themselves serving to guide the direction of flow of the hot gases.

The acetate of lime, which has already been evaporated in a pan to a paste and contains at least 40 per cent of the dry product, is delivered in the most convenient manner on to the top belt; the product falls from one belt to another, as described above, until finally it is discharged from the drying chamber by the last belt as dry acetate of lime. In another form of belt-drier the acetate paste is spread, in a very thin layer, on a single endless belt made of metal webbing, which travels over rollers and follows a zigzag path opposed to the direction of a current of hot air passing through the apparatus.

The material does not fall from one belt to another but remains in the same position on the single belt which conveys it through the drying chamber.

As a result of drying the paste in a thin layer, the final product from this form of apparatus is very light and pulverulent, and is unsuitable for conversion into acetic acid or acetone, or for transport in cheap sacks.

Numerous modifications of these mechanical plants for drying *acetate paste* are possible; none of them, however, represents a continuous drying apparatus capable of working-up *acetate liquor* to dry acetate of lime.

The various forms of apparatus described above certainly replace the drying floors, but the evaporating pans must still be used to produce the paste; hence none of the disadvantages arising from formation of scale during the process of evaporation are eliminated.

A continuous mechanical drying plant for acetate of lime can only be regarded as fully serving its purpose if it is capable of dealing directly with acetate liquor, converting it into the dry product without any formation of scale.

Recognising the importance of a really efficient continuous drying plant, the author, after an investigation extending over several years, succeeded in designing an apparatus which afforded a practical solution of the problem; apparatus of this

type has now been in successful operation on a large scale for a considerable period.

The design of this apparatus is based on the observation that acetate liquor, when spread out in thin layers on hot surfaces, dries rapidly without passing through the viscous stage at all ; the dry product may therefore be removed quite easily by scraping.

The continuous *drum-drier*, introduced by the author, takes advantage of this behaviour on the part of the acetate liquor.

The apparatus consists of a hollow steel cylinder which is heated internally by means of high-pressure steam, waste steam or waste gases, and is rotated by suitable external mechanism. The cylinder dips into a trough containing the acetate liquor, so that during rotation its entire surface becomes coated with a thin film of liquor ; this film undergoes rapid evaporation and leaves the solid acetate in the form of a grey coating on the hot surface of the cylinder. In the course of one revolution of the cylinder, this coating dries more or less completely ; before that portion of the cylinder to which the product is adhering dips again into the liquor, the coating is removed by means of scraper-blades which are held against the cylinder by means of counterweights.

This apparatus, which is very simple in itself but operates with extreme regularity and certainty, is capable of producing acetate of lime containing 80 per cent of calcium acetate directly from acetate liquor, in one single continuous operation. The product, however, is obtained in the form of a very light and fine powder which gives rise to much dust during the drying operation and is liable to escape through the cheap, rather loosely woven sacks in which it is transported ; moreover, if it is employed for the manufacture of acetic acid or acetone, further difficulties are experienced owing to its dusty nature and its tendency to agglomerate.

For these reasons the author decided to carry the drying process only so far as to ensure that the product from the drum-drier would no longer show any tendency to agglomerate or to form an adhesive mass.

In this way the formation of dust during the drying process is avoided ; if the product is then passed through a closed belt- or paddle-drier (or some similar form of apparatus) it becomes granulated and leaves the plant comparatively free from dust and above all free from scale. Fig. 38 shows a

drying plant of this type, constructed by F. H. Meyer, Hannover - Hainholz, which avoids all the objectionable features of evaporation in open pans and final treatment on drying floors.

An apparatus of this type consumes relatively small amounts of power and fuel, and requires only one man per shift to operate it ; its capital cost is comparatively low and is soon

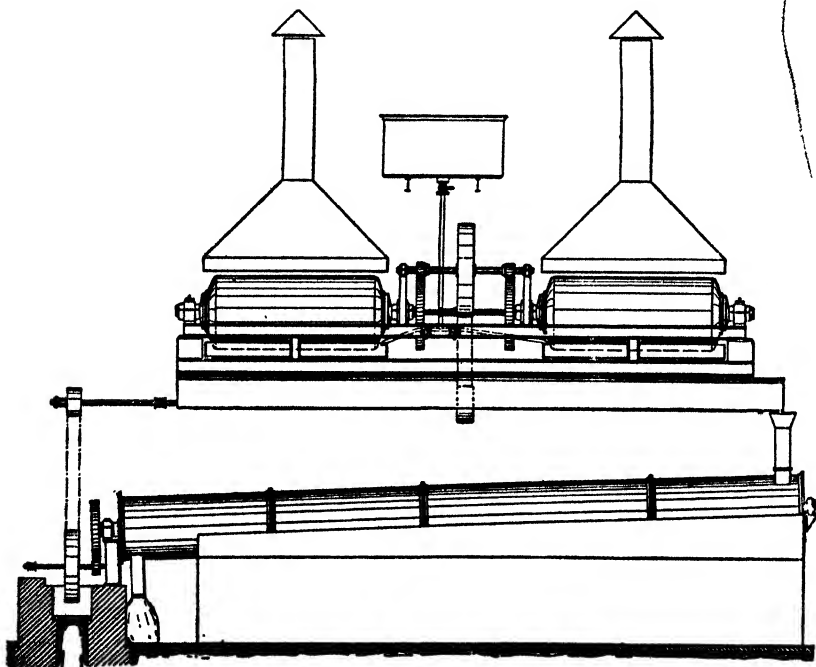


FIG. 38.—CONTINUOUS MECHANICAL DRUM-DRIER FOR THE PRODUCTION OF SOLID ACETATE OF LIME DIRECTLY FROM SOLUTION.

covered by the saving in wages, fuel, etc. ; it treats the acetate liquor continuously and efficiently ; no scale is formed on the heating surfaces, and boiling-over is impossible ; the workmen no longer have to suffer from heat, vapour and dust ; the apparatus is in no way dependent on the weather ; it is no longer necessary to lay down a drying floor composed of several hundred square metres of expensive iron plates, and the plant conforms with the official regulations regarding the evolution of injurious fumes in workshops.

There can be little doubt that before very long the open evaporating pans and drying floors will have entirely disappeared and will have been replaced by mechanical drying plant.

IV. MANUFACTURE OF SODIUM ACETATE FROM PYROLIGNEOUS ACID

Formerly, it was the usual practice for wood-distillation factories to convert their pyroligneous acid into sodium acetate, or "red salt," which was placed on the market for use in the manufacture of acetic acid and its derivatives. At the present day, however, acetic acid—whether technical acid of 30–50 per cent, or glacial acid of 96–99·5 per cent—is no longer made from sodium acetate; the latter has been almost completely superseded by the calcium salt—grey acetate of lime—and is now produced and consumed only on a very limited scale.

Sodium acetate may be manufactured from crude pyroligneous acid in exactly the same manner as grey acetate of lime, except that caustic soda is used as the neutralising agent instead of lime.

Before neutralisation the acid must be deprived of tar by a special distillation, etc.; the naphtha is then removed from the neutralised liquor, and the residual liquor—dilute sodium acetate solution—is run into settling tanks, allowed to stand for some time, and afterwards evaporated in open or closed evaporators by means of high-pressure steam, waste steam or furnace gases. When the solution is sufficiently concentrated it is run into open cast-iron hemispherical or trough-shaped pans provided with suitable stirring apparatus and heated by direct fire; in these pans the solution is evaporated to dryness. The dry mass is then heated further, with constant stirring, until it is completely dehydrated and the anhydrous salt is molten. The melting-point of the anhydrous salt is about 320° C.; not very far above this point the product begins to decompose into acetone and sodium carbonate. Overheating must therefore be avoided, otherwise serious loss may be incurred.

As a result of this melting process a much purer product is obtained. In the first place sodium propionate and butyrate, which always accompany the acetate, undergo decomposition:

at the melting-point of the latter, becoming converted into volatile ketones and sodium carbonate. At this relatively high temperature empyreumatic matter is expelled from the molten mass in the form of vapour ; other components of the tarry matter present are burnt, or become converted into charred matter which is insoluble in water and remains behind when the melt is dissolved and the solution filtered.

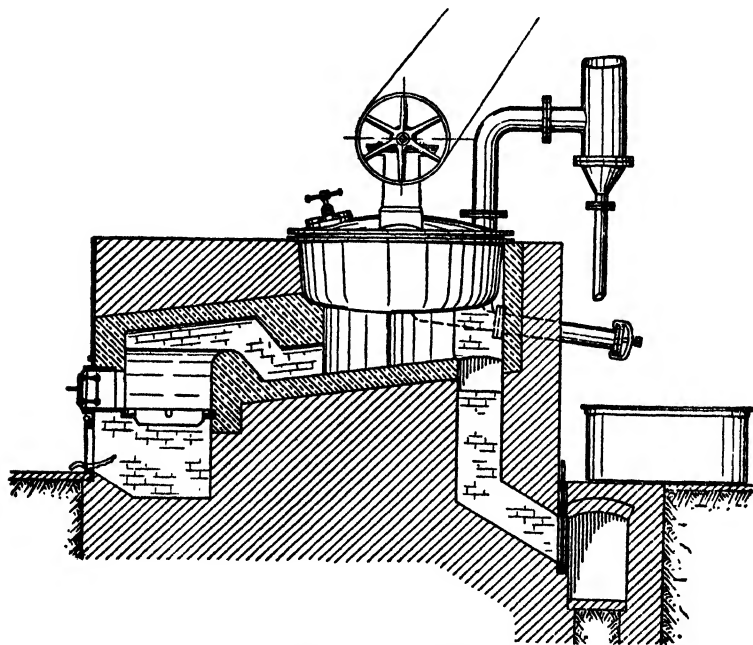


FIG. 39.—DIRECT-FIRED PAN FOR FUSING SODIUM ACETATE, FITTED WITH STIRRING APPARATUS AND AN OUTLET FOR THE ESCAPE OF FUMES.

After the salt is completely fused and foaming has ceased, the liquid is run out of the pan and allowed to cool. The solid product is again dissolved in boiling water to form a solution sufficiently concentrated to crystallise on cooling ; and the solution is passed through a filter press from which it runs directly into the crystallising tanks.

If large crystals are required, the liquor is stirred occasionally ; if small crystals are desired, the liquor must be stirred continuously with a mechanical stirrer. When the process of crystal-

lisation is completed, the crystals are separated from the mother-liquor by centrifuging.

The mother-liquor and the wash-liquors from the centrifuging and filtering processes are returned to the crude liquor awaiting evaporation.

Provided that the processes of fusion and crystallisation have been properly conducted, the crystals leaving the centrifuge are practically colourless and usually ready for sale. In certain circumstances, however, further purification must be carried out by dissolving the crystals in water, filtering the solution through a filter press and recrystallising.

Attempts have been made to remove impurities from dehydrated sodium acetate by dissolving it in water and filtering the solution through animal charcoal, instead of submitting the product to the fusion process which tends to cause loss.

This method, however—like all others which have been suggested—offers no advantages over the fusion process, which is easily carried out and gives more certain results.

The method described above for the manufacture of sodium acetate directly from pyroligneous acid can only be employed, of course, in a wood-distillation factory.

If the product is to be manufactured elsewhere two processes are available :—

1. Manufacture from acetate of lime.
2. Manufacture from the weak fractions (first runnings) obtained in the manufacture of acetic acid by the sulphuric acid process.

V. SODIUM ACETATE FROM ACETATE OF LIME

Formerly, sodium acetate was prepared from acetate of lime by double decomposition with sodium sulphate. This method, however, is very complicated, since the calcium sulphate, which is a product of the reaction, is fairly soluble in the acetate solution ; as a result, the acetate is rendered impure and the presence of the sulphate also interferes with the crystallisation of the product.

Another process, which is distinctly superior, consists in decomposing acetate of lime in aqueous solution with sodium carbonate. The decomposition is carried out in wooden vats

fitted with stirring apparatus ; calcium carbonate separates out and sodium acetate remains in solution. The liquor is passed through a filter press, and the clear solution of sodium acetate is then treated in exactly the same manner as the solution obtained by neutralising tar-free pyroligneous acid with caustic soda (see above).

VI. SODIUM ACETATE FROM ACETIC ACID

During the rectification of crude acetic acid, fractions containing only 12-20 per cent of acetic acid, and possibly even less, are obtained. Owing to their low concentration it is difficult to find an outlet for these products, but they are quite suitable as raw material for the manufacture of sodium acetate. The process is carried out in a simple manner by neutralising the weak acid with ammonia-soda in wooden vats. The soda is added in slight excess, in order to remove any traces of copper which may be present in the acid and which would tend to impart a green colouration to the crystals of sodium acetate. The precipitate of basic copper carbonate is separated from the solution of sodium acetate in a filter press and thoroughly washed. The acetate solution is evaporated to the necessary concentration in tinned copper pans fitted with steam coils. The concentrated liquor is then acidified and run from the pan into the crystallising tank. After crystallisation the mother-liquor is removed, and the crystals are thrown on to a sloping board covered with sheet lead, which lies in front of the tank, in order to free the crystals still further from the mother-liquor. The drained crystals are then passed through a centrifuge, after which they are usually packed for shipment, either without further treatment or else after a short final drying in a drying room.

VII. MANUFACTURE OF "IRON LIQUOR"

The product known as "iron liquor" consists essentially of an aqueous solution of ferrous acetate, and is largely used as a mordant for certain classes of dyestuff. Several of the smaller English and Scotch wood-distillation factories which are only very primitively equipped convert the whole of their output of pyroligneous acid into this product.

"Iron liquor" is manufactured by allowing settled crude

pyroligneous acid, from which the naphtha has been removed by distillation, to flow through vessels filled with iron turnings, iron filings or scrap iron. Hydrogen is evolved, and a certain amount of tarry matter which settles out on the surface of the liquor is removed by skimming. The liquor is allowed to remain in contact with the iron until the evolution of hydrogen has ceased; it is then evaporated to the required concentration.

The liquor is usually sold at two different strengths, namely, 24° Tw. (sp. gr. 1.12) and 32° Tw. (sp. gr. 1.16); it is said to be more suitable for use as a mordant if it contains a small quantity of free acetic acid.

An analysis of a typical commercial "iron liquor" gave the following figures:—

	Per cent.
Combined acetic acid	10.93
Free " "	0.03
Ferrous oxide	6.39
Ferric oxide	0.16
Total iron as Fe_2O_3	7.27
Matter in suspension	0.01

CHAPTER XVI

PRODUCTION OF ACETIC ACID AND ACETONE FROM ACETATE OF LIME

I. MANUFACTURE OF ACETIC ACID FROM GREY ACETATE OF LIME

As a general rule the smaller wood-distillation factories do not undertake the further treatment of acetate of lime, since the conversion of only small quantities of that product into acetic acid is usually unprofitable.

It is much more common for these factories to sell their output of acetate to concerns which are engaged specially in the production of acetic acid.

In former times, when the demand for acetic acid was still quite small, but the price which it commanded was comparatively high, even small factories undertook the manufacture of the acid and found it a profitable business. In those days acetate of lime was not used directly for the production of the acid but was converted into sodium acetate by a more or less complicated process; or else, pyroligneous acid was worked up directly into sodium acetate, this product was dehydrated, and pure acetic acid was then obtained by treating the anhydrous salt with sulphuric acid.

If we completely disregard certain still older methods of manufacture, the decomposition of anhydrous sodium acetate afforded the only means of preparing highly concentrated acetic acid; on the other hand, acetic acid with a concentration of 50 per cent or less was already manufactured at an earlier period by decomposing acetate of lime with hydrochloric acid.

Except when pure sodium acetate was used as the raw material these products were by no means pure, hence it was quite out of the question to utilise them—after suitable dilution—as vinegar.

The progress which had been made in the spirit industry

result of the introduction of column stills suggested the application of these stills in suitably modified form to the acetic acid process. Experiments were carried out on these lines at the beginning of 1870, and it was found possible, by simple rectification, to produce absolutely pure glacial acetic acid (96-99.5 per cent) from crude acid obtained by decomposing acetate of lime. After this achievement the industry developed rapidly, and an unusually wide market for acetic acid was created. The success which has attended the introduction of diluted, chemically pure acetic acid for edible purposes is best indicated by the hard fight which has been carried on constantly against "wood-vinegar" by the manufacturers of malt-vinegar; but quite apart from its use as vinegar, acetic acid and its derivatives (acetic anhydride, etc.) are consumed in large quantities by the textile and chemical industries, for example, in the manufacture of artificial indigo.

As mentioned above, two methods are available at present for the manufacture of acetic acid from wood-distillation products. The older method, which is only rarely used nowadays, consists in decomposing pure anhydrous sodium acetate with concentrated sulphuric acid.

In this process the acetate is treated with sulphuric acid in cast-iron or copper apparatus heated by steam or direct fire. The strength of the product varies from 80 to 90 per cent, according to the concentration of the sulphuric acid, the moisture content of the sodium acetate, and the relative proportions in which these raw materials are present. The product still contains sulphur dioxide and must be purified by a second distillation in the presence of oxidising agents.

During a considerable period, prior to the recent introduction of synthetic processes of manufacture, the whole of the acetic acid of commerce was obtained exclusively from grey acetate of lime containing 80-82 per cent of calcium acetate, as put on the market by the wood-distillation factories.

Grey acetate of lime possesses the following approximate composition:—

	Per cent
Calcium acetate (including calcium propionate butyrate, etc.)	82
Water	10
Foreign matter, mostly of organic nature	8

Two methods are available for the manufacture of acetic acid from this product :—

1. Decomposition with hydrochloric acid.
2. Decomposition with sulphuric acid.

Both methods are in use, the choice depending on the particular quality of acetic acid which it is desired to produce, and above all on the relative prices of hydrochloric acid and sulphuric acid. As a general rule hydrochloric acid cannot compete in price with sulphuric acid ; moreover, the hydrochloric acid process produces much less glacial acetic acid (96–99·5 per cent) and a much larger quantity of weak acid (30–50 per cent). In view of the fact that the weak commercial qualities command a lower price per unit (1 kilo. per cent) of acetic acid than the glacial acid, and also that it is much easier to sell glacial acid (96–99·5 per cent) and vinegar essence (80 per cent) than weak commercial acid, it will be obvious that in present-day conditions the hydrochloric acid process cannot possess very great importance. It must be noted also that this process entails heavy charges for depreciation and maintenance owing to the intense action of the acid on the plant.

On the other hand, the hydrochloric acid process offers the advantage that it can be used with all qualities of acetate of lime (grey or brown acetate), whereas the ordinary sulphuric acid process cannot be used with brown acetate (67 per cent calcium acetate) owing to the presence in the latter of a large amount of tarry matter. Hence the acetic acid manufacturer, if restricted to brown acetate of lime, is compelled to use the hydrochloric acid process, or else to carry out the decomposition of the acetate with dilute sulphuric acid (60° Bé or less).

1. Hydrochloric Acid Process.—It is possible to apply this process in two different ways :—

- (a) Decomposition with aqueous hydrochloric acid ; the recovery of the acetic acid resulting from this reaction may be carried out either *intermittently* or *continuously*.
- (b) Decomposition with gaseous hydrochloric acid.

Decomposition with aqueous hydrochloric acid, and subsequent recovery of acetic acid by an *intermittent* process, is probably the oldest method of obtaining acetic acid from

acetate of lime. It is carried out by treating the acetate with the necessary quantity of hydrochloric acid in wooden vats, with or without a lead lining, or in brickwork pits. In either case wooden stirring apparatus is provided. Fig. 40 shows a plant of this type.

As a rule 110 kilos. of hydrochloric acid (20–21° Bé) are sufficient for the decomposition of 100 kilos. of acetate of lime. After the raw materials have been introduced into the vats, the mixture is stirred thoroughly until it is completely liquid; it is then allowed to stand for some time. A layer of tar separates out on the surface of the liquid, and carries with it any

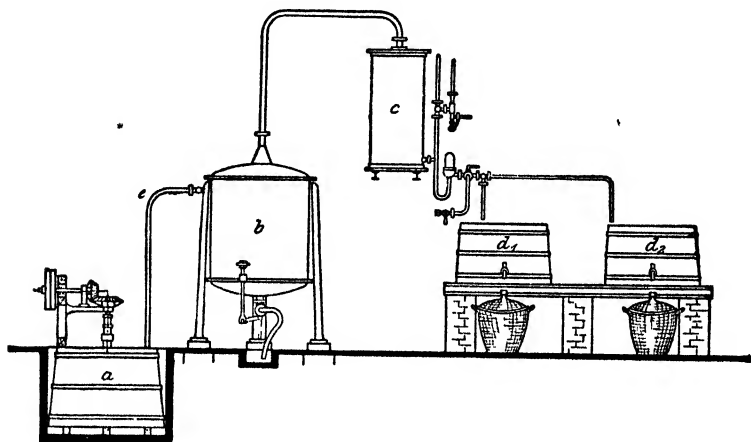


FIG. 40.—APPARATUS FOR THE MANUFACTURE OF ACETIC ACID BY THE ACTION OF CRUDE HYDROCHLORIC ACID ON ACETATE OF LIME.

a, mixing vat; *b*, copper still; *c*, condenser; *d*₁, *d*₂, collecting vats; *e*, suction pipe.

mechanical impurities which may be present, such as particles of wood, straw, etc. This layer is removed, and the clean liquor, which consists of a mixture of calcium chloride and acetic acid in aqueous solution (specific gravity about 1.254), is run into a distillation apparatus as shown in Fig. 40. This apparatus consists of a copper vessel fitted with open and closed steam-coils. The vessel is connected by a delivery pipe of suitable width with a condenser made of seamless copper piping, the outlet of which delivers into a wooden collecting vat; or else, the acid issuing from the condenser may be led directly into carboys.

The simplest method of charging the still is to evacuate it by means of a steam ejector which is connected preferably with the condenser outlet-pipe. After evacuation the cock on the suction pipe dipping into the mixing vat is opened, and the reaction mixture flows rapidly into the still. The use of pumps, which for this purpose are unsuitable since they become blocked up very quickly, is thus entirely avoided. If all joints of the still are brazed, and afterwards further hardened by hammering, the life of an apparatus of this kind is fairly long. The durability of the apparatus also depends on the quality of the hydrochloric acid used. Experience has shown that the presence of arsenic, particularly, in the acid leads to very rapid corrosion of the metal surfaces.

Cast-iron stills lined with clay tiles have not proved particularly serviceable either for this process or for the subsequent process of rectification.

After the still is charged and the air-pressure has been equalised by opening the air-cock, heating is begun with the closed coil—that is, by indirect steam. From the outset the acid distilling over is “water-white” or possesses, at the most, a yellowish tint. A volume equivalent to about 50 per cent of the original charge can be distilled over without any difficulty; by this time the calcium chloride liquor has become highly concentrated, and on further heating by indirect steam gives off only very little acid; it is advisable, therefore, when this stage is reached, to introduce direct steam, which drives over a further amount of acid but at the same time, of course, reduces the concentration of the distillate. If an almost water-white distillate free from chlorine is desired, the product is redistilled, usually with the addition of a certain amount of soda to combine with any free hydrochloric acid present; the acetic acid obtained as a result of the second distillation is usually quite suitable for all technical purposes.

Theoretically, about 61–62 kilos. of absolute acetic acid should be obtained from 100 kilos. of acetate of lime at 82 per cent. This yield, however, is never attained, since the calcium chloride liquor remaining in the still always retains a certain amount of acid which is not worth the cost of recovery. As a general rule the product is not submitted to any further treatment but is simply put on the market at the particular strength with which it leaves the process. It is quite practicable, however, to work up the product, which contains

on an average about 45 per cent acetic acid, to chemically pure acid at 80–100 per cent. The method of performing this operation and the nature of the plant employed are described below.

The Continuous Hydrochloric Acid Process¹ (see 1a above).

—The continuous process is carried out by treating acetate of lime with hydrochloric acid in the manner already described, and then delivering the reaction-mixture continuously to the distillation plant. The latter consists of a column which contains a number of plates and is fitted with suitable heating arrangements. The preheated acid liquor is delivered continuously on to the top plate of the column; it runs down the column from plate to plate and during its passage gives off acetic acid in the form of vapour. The vapour rises to the top of the column and passes into a condenser; the exhausted calcium chloride liquor is discharged continuously from the bottom plate of the column.

Compared with the intermittent process, the continuous process would appear to offer considerable advantages, particularly in the matter of general working costs.

It has been found, however, that this process causes great wear and tear of the plant and produces an impure and relatively weak distillate, thus wiping out the advantages which it may afford in other directions. At any rate, the continuous process has not come into general use, probably owing to its own particular nature and to the fact that in any case the hydrochloric acid process is scarcely in a position to compete with the sulphuric acid process.

(b) Decomposition of Acetate of Lime with Gaseous Hydrochloric Acid.—A great disadvantage attaching to the use of aqueous hydrochloric acid is that the strength of the crude acetic acid resulting from the reaction rarely exceeds 45 per cent; in consequence only a relatively low yield of glacial acetic acid—the most valuable product—can be obtained from the crude acid. By decomposing acetate of lime with *gaseous* hydrochloric acid, however, it is possible to obtain a crude product which in respect of concentration approaches considerably nearer to the crude acid from the sulphuric acid process but still does not equal it. The process was first described in the Austro-Hungarian Patent No. 12,421. It is carried out, according to this patent, by introducing

¹ German patent [118,608.

acetate of lime free from dust into vertical retorts which are heated externally. A current of hydrochloric acid gas, possibly superheated beforehand, is then passed in, and the products from the retorts are condensed in the usual manner.

Attempts have also been made to produce acetic acid in a similar manner by utilising gaseous hydrochloric acid obtained as a by-product in other processes, but the results have never been as good as those obtainable by the sulphuric acid process, and the cost of working the process is higher. The wear and tear of the plant is considerable, and the crude acetic acid produced is highly contaminated with hydrochloric acid; moreover, the subsequent treatment of this product for chemically pure acetic acid is by no means as simple as that of the crude acid obtained in the sulphuric acid process. In most cases where gaseous hydrochloric acid occurs as a by-product it should be sounder practice to absorb the gas in water and sell it in the form of aqueous hydrochloric acid, for at present a good demand exists for this product and it commands a good price.

2. Sulphuric Acid Process.—Up to 1870 the hydrochloric acid process was used almost exclusively, but since that time the sulphuric acid process has been generally introduced into nearly all acetic acid factories, both in Germany and elsewhere. This process differs from the hydrochloric acid process not only in the agent used but also in the method of operation and in the results obtained. In the hydrochloric acid process it is generally unnecessary to use stirring apparatus, since the reaction-mixture remains liquid even after the acetic acid has been driven off, and thus allows the acid to escape quite readily apart from a small unavoidable residue. In the sulphuric acid process, however, it is necessary to provide very stoutly constructed stirring apparatus for use during the operation of decomposing the acetate of lime, since the resulting mixture forms a solid mass which only gives off acetic acid in a satisfactory manner if it is stirred. In the hydrochloric acid process scarcely any secondary reactions occur, owing partly to the fact that decomposition is carried out with an aqueous solution of the acid; the water present dilutes the mixture to a certain extent and the reaction is less vigorous accordingly. In the sulphuric acid process, however, both raw materials are used in concentrated form.

As already mentioned, acetate of lime contains certain

organic impurities (aldehyde-resins, etc.). During the decomposition process a considerable amount of heat is evolved, which causes these impurities to react with a portion of the sulphuric acid, reducing it to sulphurous acid; the latter then passes over with the distillate, accompanied by certain other volatile by-products which are formed during the reaction. Hence the crude acid obtained in the sulphuric acid process is always less pure than that from the hydrochloric acid process, but it possesses the advantage of being much more highly concentrated. We may assume that 60 kilos. of sulphuric acid at 66° Bé are required for the decomposition of 100 kilos. of acetate of lime containing 82 per cent of calcium acetate and 10 per cent of water, and that the crude product of the reaction will contain 59 kilos. of absolute acetic acid. The yield of crude acid will then be represented by the sum of this weight of absolute acetic acid and the weights of water which are present in the acetate of lime and sulphuric acid respectively and pass over in the distillate, that is,

$$59 + 10 + 4.8 = 73.8 \text{ kilos.}$$

It follows that the concentration of the crude acid must amount to:—

$$\frac{59 \times 100}{73.8} = \text{approx. } 80 \text{ per cent.}$$

This is the highest concentration attainable when the raw materials used are acetate of lime containing 10 per cent of water, and sulphuric acid at 66° Bé.

In practice it is actually possible by means of the sulphuric acid process to obtain a crude product containing 80 per cent of organic acids reckoned as acetic acid.

The sulphuric acid process is carried out by allowing the concentrated acid (usually 92 per cent = 66° Bé) to act on grey acetate of lime. The reaction must be furthered by efficient stirring which will ensure that the acid is thoroughly incorporated with the acetate.

The reaction, which is exothermic, results in the liberation of acetic acid and other organic acids, and the formation of calcium sulphate; at the same time the resinous or pitch-like matter present in the acetate separates out. During this process the reaction-mixture forms a more or less pasty mass in which, if the stirring is insufficient, calcium sulphate, acetate

of lime, free sulphuric acid and resinous matter may exist side by side.

During the process of decomposition the acetate of lime becomes coated with a layer of calcium sulphate, the organic acids are vaporised by the heat of reaction, and the organic impurities separate out. The heat of reaction causes these impurities to react more or less, according to the temperature, with the free sulphuric acid, reducing it to sulphurous acid.

The extent of this secondary reaction depends, therefore, on the temperature of the reaction-mixture and on the efficiency of the stirring apparatus or, in other words, the degree of intimacy with which the calcium acetate and sulphuric acid are mixed.

By employing properly constructed stirring apparatus which is rotated at a suitable speed, and by regulating the amount of reaction-mixture in accordance with the capacity of the stirring apparatus, the danger of secondary reactions taking place as a result of insufficient mixing can certainly be reduced though not entirely eliminated.

On the other hand, by keeping the temperature of the reaction-mixture sufficiently low it is possible almost completely to prevent the impurities from exercising a reducing action on any free sulphuric acid which may be present, even if the mixing is insufficient in certain parts of the mass.

Reduction of sulphuric acid to sulphur dioxide and water causes a loss of material, since the former escapes from the mixture immediately, and finds no opportunity to act on any considerable quantity of acetate of lime. Hence, in order to make up for this loss an excess of sulphuric acid must be employed.

The water formed by the reduction of sulphuric acid mixes with the distillate and dilutes it to a certain extent.

It is obvious, therefore, that in carrying out this process care must be taken to avoid as far as possible introducing conditions which will favour the reduction of the sulphuric acid by organic impurities.

As long as properly constructed stirring apparatus is provided and a sufficiently low temperature is maintained during the reaction, decomposition of the acetate proceeds quite satisfactorily.

At first the reaction-mixture is pulverulent, but after a short time it changes into a paste which can be easily stirred.

Gradually the mass becomes more and more viscous and putty-like owing to hydration of the calcium sulphate, and at this stage considerable power is required to knead it thoroughly. After going through the viscous stage the mass again becomes pulverulent and dry, and in this state offers much less resistance to the stirring apparatus.

The amount of heat liberated during the reaction is sufficient to distil over a large proportion of the organic acids (acetic acid and its homologues) from the reaction-vessel into the condenser. This takes place chiefly during the pasty and viscous stages.

When the mass has reached the final pulverulent stage, at which it is more voluminous than at the preceding stages, expulsion of the acid still present becomes much more difficult. If high-pressure steam at a temperature of about 160°C . is used as the heating agent, it is found that this temperature does not suffice to expel the last traces of acetic acid from the residue—at any rate, not if the distillation is carried out under atmospheric pressure—although the boiling point of acetic acid is only 118°C . It is necessary, therefore, to adopt special measures for overcoming this difficulty.

The process of decomposing acetate of lime with sulphuric acid thus resolves itself into two distinct phases, namely:—

1. Decomposition of the acetate, resulting in the liberation of acetic acid and its homologues, and the formation of calcium sulphate; during this phase, acetate of lime, calcium sulphate, free sulphuric acid, free organic acids and certain organic impurities exist side by side.

2. Distillation of the free volatile acids from the residual calcium sulphate, after complete equilibrium has been attained in the mixture.

The essential conditions for the first phase are thorough mixing and a low temperature; for the second phase a relatively high temperature.

The residual calcium sulphate contains calcium sulphite and even sulphide, which are formed as a result of secondary reducing actions, to an extent depending on the temperature prevailing in the reaction-mixture during the first phase of the process. Small quantities of sulphuric acid and acetate of lime are also present in the residue.

When direct-fired apparatus is employed, a further process may occur if the mixing is inefficient and the temperature is

allowed to become too high, namely, direct decomposition of the acetate into acetone and calcium carbonate.

It will be obvious, therefore, from what has already been stated, that the sulphuric acid process is not as simple as may appear at first sight.

In view of the conditions which must be observed in conducting the process, it follows that the method of supplying heat to the plant is a matter of the highest importance. Before dealing with the apparatus used in the modern sulphuric acid process we may consider briefly the various heating agents which have been adopted or suggested, namely :—

1. Direct fire, using either an ordinary grate-furnace (plane grate, step grate, etc.), a semi-gas fired, or a gas-fired furnace.
2. Baths of various kinds.
3. Superheated air or gas.
4. Superheated water.
5. High-pressure or superheated steam.

We have seen above that the first phase of the process requires a low temperature and the second phase a high temperature. It must be possible, therefore, as soon as one operation is completed, to reduce the temperature of the apparatus rapidly, so that the next operation may be begun.

Direct-fired apparatus satisfies this requirement least of all. The reaction-vessel must always be built into a furnace, the brickwork of which gradually becomes more or less incandescent and therefore continues to radiate heat long after firing has ceased.

In consequence it is difficult to keep the temperature of the reaction-mixture sufficiently low during the first phase of the process ; as a result the sulphuric acid undergoes reduction to sulphur dioxide and water, and possibly to hydrogen sulphide. Further, a certain amount of acetate of lime is decomposed directly to form acetone. In apparatus of this type reduction of sulphuric acid is so pronounced that instead of 53·9 kilos. of sulphuric acid—the amount required theoretically to decompose 100 kilos. of acetate of lime—about 70 kilos., that is, 130 per cent of the theoretical amount, must be supplied. Moreover, the crude acetic acid obtained by this process is very impure ; it contains only 72 per cent, instead of a possible 80 per cent, of organic acids, and is highly contaminated with sulphur dioxide and hydrogen sulphide. The removal of these

impurities is attended by further disadvantages, and the yield of glacial acetic acid is essentially lower than that from an 80 per cent crude acid, which contains very little, if any, sulphur dioxide.

It is obvious, therefore, that direct-fired apparatus cannot be regarded as the ideal form of plant for the decomposition of acetate of lime with sulphuric acid.

The use of some form of *bath* for heating the reaction-vessel only requires very brief consideration. Easily fusible metals, fats, high-boiling hydrocarbons, etc., might be employed for the purpose. Here again it is impossible to secure sufficiently rapid cooling between one operation and the next, at least by any methods suited to actual practice. Moreover, the rate of transfer of heat from baths of this type is very slow owing to lack of sufficient circulation, and the temperature difference is naturally much lower than that attained by employing direct fire. The performance of apparatus heated in this manner is therefore lower than that of direct-fired plant, and many of the drawbacks attaching to the latter are again present ; for these reasons the use of baths for heating the reaction-vessels cannot be seriously considered.

Hot air or some other *hot gas* would appear to be a much more convenient heating agent. In this case the reaction-vessel would consist of a jacketed pan, and no brickwork setting would be required. The air would be forced by a blower, compressor or similar apparatus through a superheater, in which it would be heated to a definite temperature ; from the superheater it would pass through pipes to the reaction-vessel, and having transferred its heat through the walls of the vessel to the charge it would return to the blower and again be circulated through the system.

A heating arrangement of this type would fulfil all the above-mentioned conditions and should therefore be applicable to the process, but such plant is complicated and is not particularly easy to operate. Moreover, the coefficient of transmission of heat from hot air to the slowly moving pulverulent material in the vessel is low—only about 10 kilocalories per hour for 1 sq. m. of heating surface and 1° C. difference in temperature ; hence the performance of apparatus heated in this manner would be low, and the capital cost would be relatively high as in the case of apparatus heated by a bath.

In recent years *superheated water* has been adopted as a heating agent for many processes requiring the use of high, uniform temperatures which can be easily controlled. Superheated water plant is very similar to the ordinary hot-water heating apparatus—that is, the water circulates in a closed pipe system, the furnace being situated at the bottom of the system. In hot-water heaters, however, the temperature can never exceed $100^{\circ}\text{C}.$, whereas in a superheated water system the temperature may reach $350^{\circ}\text{C}.$ With this high temperature the internal pressure in the system is naturally very considerable, a factor which, taken in conjunction with the high capital cost of the plant, partly accounts for the fact that this type of heating apparatus has not been generally adopted by the acetic acid industry, although it is capable of fulfilling all the requirements in regard to regulation of temperature during the process of decomposing the acetate.

These disadvantages, however, would not necessarily render the use of superheated water plant prohibitive if a better method of heating were not available, and the same may be said of all the other systems which have been described above. By employing *high-pressure steam* it is possible to secure all the advantages of heating with superheated water, without any of its disadvantages.

As regards the possible use of *superheated steam* it is only necessary to remark that, however suitable it may be for direct heating, this agent has never proved of any value for the purpose of transmitting heat indirectly through the medium of a metal partition, owing to the fact that in properties it closely resembles a gas.

Hence the only agent which remains to be considered is *high-pressure steam* (6–8 atm.).

As mentioned above, it is impossible by using high-pressure steam (temp. $160^{\circ}\text{C}.$) to distil over the last traces of acetic acid from the residue of calcium sulphate. This residue, which occludes the residual acetic acid, possesses such low thermal conductivity that the difference between the temperature of the heating agent ($160^{\circ}\text{C}.$) and the boiling-point of the acetic acid (118°) is not sufficiently great for the purpose, in spite of the fact that the coefficient of transmission of heat from steam to the contents of the vessel is large—namely, about 800 kilo-calories.

It is possible, however, by maintaining a reduced pressure in the apparatus during the distillation process, to increase the difference in temperature between the heating agent and the contents of the vessel from 40° to 90°C. , since the boiling-point of acetic acid *in vacuo* is only 70°C. Experience has proved that in these conditions practically the whole of the acetic acid may be distilled over from the residue of calcium sulphate.

The *vacuum distillation process*, which was introduced in 1895, not only superseded the direct-fired plant, which hitherto had been used almost exclusively, but it also permitted the construction of larger apparatus which made it possible to treat 1500 kilos. or more of acetate in one charge, instead of only 300 kilos. as was previously the case.

In view of the simple nature of a steam-heated apparatus, and the fact that an apparatus of this type produces the highest yields of acetic acid obtainable by the sulphuric acid process at a low cost for operation, it will readily be understood that none of the other processes mentioned above is in a position to compete with the vacuum process, since no other method of heating the reaction-vessel surpasses the use of steam in respect of simplicity and cheapness, or yield and quality of the product.

The credit of having introduced the vacuum process¹ into the acetic acid industry is due to K. v. d. Linde, though it had already been applied in a somewhat different form by various firms before this patent was granted.

Linde recognised that when steam is used as a heating agent it is only possible to distil off acetic acid quantitatively from the residual calcium sulphate provided that a very low pressure—less than 160 mm.—prevails inside the plant, whereas before Linde applied for his patent a higher degree of pressure, which was naturally less effective, had been employed.

By adopting the vacuum process Linde was able to obtain an almost quantitative yield of acetic acid from the action of sulphuric acid on acetate of lime, and at the same time to render possible the use of steam as a heating agent. Behrens² sought to achieve this object by carrying out the process of decomposition in such conditions that the possibility of free sulphuric acid existing in the reaction-mixture was excluded, or at least that reduction of the acid was rendered impossible.

Behrens based his process on the old chemical axiom:

¹ German patent 92,418.

² German patent 12,199.

"Corpora non agunt nisi fluida," and therefore dissolved the acetate of lime in a suitable solvent before the addition of sulphuric acid. It is obvious that the only solvent which could be considered in this connection was acetic acid itself.

The acetate is dissolved in acetic acid of certain definite concentration first of all, and the amount of sulphuric acid necessary for liberating the organic acids is then added to the solution.

The whole reaction proceeds under dilution, and in these conditions the possibility of the sulphuric acid becoming reduced by the organic impurities present in the acetate of lime is completely excluded.

The reaction between acetate of lime and sulphuric acid is therefore almost quantitative, and the yield of acetic acid obtained by this process is equal to that from the Linde process; moreover, the Behrens process is less complicated in so far that it does not require the use of vacuum apparatus and can be carried out in any simple form of plant, which may be heated by direct fire if desired.

Later, Behrens altered his process in the sense that, instead of dissolving the acetate in acetic acid, he diluted the sulphuric acid with acetic acid in the first place, and used the mixture for decomposing the acetate.

As modified in this manner the process still offers the same advantages as before; further, the hydration of the sulphuric acid, which gives rise to vigorous evolution of heat, takes place *before* the addition of the sulphuric acid to the acetate of lime, hence the first phase of the process can be carried out with ease and rapidity at a low temperature.

Attempts have been made to obtain a still more highly concentrated crude acetic acid and therefore higher yields of the most valuable final product—glacial acetic acid—by completely dehydrating the acetate of lime before using it for the process. These attempts have always failed, for the simple reason that the one molecule of water of crystallisation present in the acetate cannot be expelled at a temperature below that at which decomposition of the acetate sets in with formation of acetone.

Both the Linde and the Behrens processes produce crude acetic acid containing 80 per cent of volatile acids reckoned as acetic acid.

Whereas the Linde process and other processes based on the

use of reduced pressure furnish the crude acid direct from acetate of lime and concentrated sulphuric acid, the Behrens process requires the addition of a third component—namely, acetic acid. The manufacturer is compelled, therefore, to introduce repeatedly into the process an already finished product—a condition which naturally entails loss. Moreover, the Behrens process involves a larger number of separate operations, in particular the dilution of the sulphuric acid or the preparation of the solution of acetate of lime in acetic acid.

Since the general results of the Behrens process are in no way superior to those of the vacuum process, which is really simpler to operate, it will be understood why the former has not been adopted by the acetic acid industry except in quite isolated cases.

In that industry the vacuum sulphuric acid process has now superseded all other processes; it represents the best method by far for the manufacture of crude acetic acid of the highest possible concentration from commercial grey acetate of lime; and nowadays it would be difficult to find an acetic acid factory of any importance which does not employ it in one form or another.

No other processes which have been suggested—for example, decomposition of acetate of lime by means of sulphur dioxide, polysulphates, bisulphate, etc.—have been adopted in practice; accordingly, only the vacuum process will be treated in detail here.

The vacuum sulphuric acid process is carried out in cast-iron vessels constructed to contain charges of acetate of lime varying from 200 to 1500 kilos. The particular form of apparatus and the nature of the heating arrangements are governed by the size of the charge.

The smaller plant consists of a dish-shaped cast-iron vessel provided with a cast-iron cover and a stoutly constructed cast-iron stirring apparatus (Fig. 41.) The dish is surrounded by an outer steel jacket forming a double bottom within which the steam used as the heating agent circulates. The acetate of lime is introduced through the open manhole in the cover. The residue is discharged either through the same manhole by means of a scoop, or else through a manhole at the bottom or in the side of the apparatus, simply by rotating the stirring apparatus. The latter form is preferable.

In apparatus designed for larger charges it is no longer

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practicable to employ jacketed cast-iron pans since the diameter is much too great.

In the larger plants the reaction-vessel is provided with a shallow cast-iron bottom containing heating channels or heating pockets, which ensure efficient heating without the risk attaching to the use of large cast-iron jacketed pans.

The wall of the vessel consists of a cylindrical cast-iron rim which is bolted on to the cast-iron bottom ; if the plant is of large capacity this portion of the vessel is also furnished with heating channels.

The manhole for discharging the residue is situated in the wall at a short distance from the bottom of the vessel.

The cover is made of cast-iron, and is provided with a manhole for introducing the acetate of lime and also with an opening for running-in the sulphuric acid ; it carries the driving gear for the stirrer, and the copper delivery pipe connecting the vessel with the condenser.

This delivery pipe is designed to act as a dust-trap for preventing the passage of acetate or calcium sulphate dust into the condenser.

The condenser is usually constructed of copper, since lead possesses only low mechanical durability. The worm or coil condenser has always proved the best type for this purpose.

The condenser is connected with an airtight receiver made of copper or earthenware, which is connected in turn with the vacuum pump, the air-chamber of which must be constructed of bronze. A scrubber is installed between the air-pump and the receiver for the purpose of extracting any traces of acetic acid which may be carried over with the air, thus protecting the pump. The measuring vessel for sulphuric acid is placed in a convenient situation above the apparatus.

In carrying out the process the charge of grey acetate of lime is introduced through the manhole in the cover ; the stirring apparatus is rotated at the same time in order to distribute the charge uniformly inside the vessel. The manhole is then closed and the sulphuric acid, which has previously been weighed or measured in the measuring vessel, is allowed to flow in gradually.

During the first phase, that is, before all the sulphuric acid is added and decomposition of the acetate is complete, it is unnecessary to use reduced pressure, since a large proportion of the liberated organic acids is distilled over by the heat

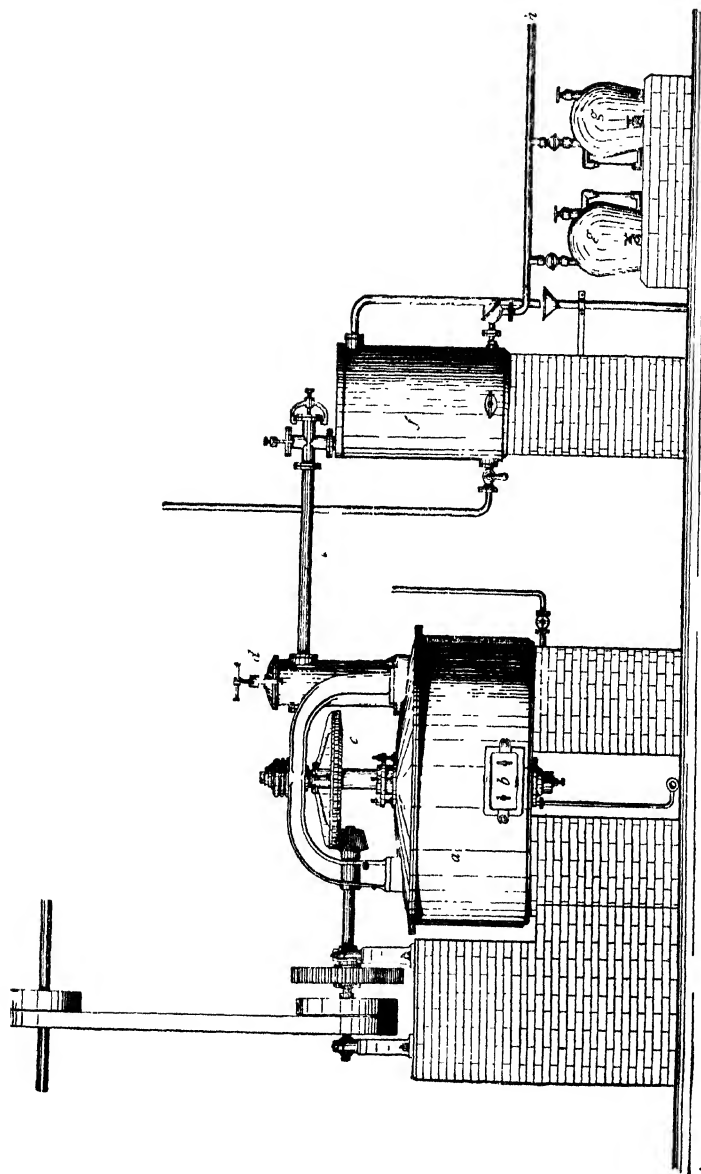


FIG. 41.—APPARATUS FOR THE MANUFACTURE OF CRUDE ACETIC ACID BY THE ACTION OF CONCENTRATED SULPHURIC ACID ON ACETATE OF LIME.

a, reaction-vessel ; *b*, discharge manhole ; *c*, stirring mechanism ; *d*, dust-trap ; *e*, delivery pipe ; *f*, condenser ; *g*, receivers ; *h*, connecting pipe to air-pump.

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of reaction, and after condensing collects in the receiver. When all the sulphuric acid has been added and distillation has slackened, the pressure inside the apparatus is gradually reduced and the distillation is completed under these conditions. The residue, which consists of calcium sulphate together with a certain amount of sulphite, sulphide, free sulphuric acid, traces of acetate of lime, etc., is then discharged through the lower manhole by rotating the stirring apparatus. It is necessary to analyse the residue for free and combined acetic acid; the lower the values obtained, the greater has been the efficiency of the process.

The complete operation occupies from three to twelve hours, according to the size of the charge, size and efficiency of the heating surfaces, the efficiency of the stirring apparatus, the pressure, and the temperature of the steam used for heating. In normal conditions 100 kilos. of acetate of lime, on treatment with 60 kilos. of sulphuric acid (66° B \acute{e}), give about 74–75 kilos. of *crude acetic acid*: this contains 80 per cent of organic acids reckoned as acetic acid, 0.005–0.05 per cent of sulphur dioxide and traces of sulphuric acid. If a copper condenser has been employed, the product also contains traces of copper. This product usually possesses a yellowish or brownish colour, owing to the presence in solution of small quantities of acetate or residue which have been carried over with the distillate; it also contains a small amount of suspended mineral matter.

Owing to its yellow colouration this product finds only a limited application, chiefly as raw material for the preparation of derivatives of acetic acid, such as ethyl acetate, amyl acetate, etc.

In the textile industry the crude acid meets with very little demand, not merely because of its colouration but owing to the presence of traces of mineral acid. Even if it is rendered colourless, as is possible by installing efficient separators between the reaction-vessel and the condenser, the demand is no greater.

These separators certainly serve to prevent the passage of mineral matter into the distillate, and to precipitate a portion of the less volatile of the products which are responsible for the colouration of the distillate, but they do not render possible the production of *crude acetic acid* completely free from mineral acid.

For this reason it is the general practice to submit the crude acetic acid to simple redistillation in a copper still provided with a copper steam-coil and connected with a condenser usually of silver.

Earthenware condensers—in fact earthenware and stoneware apparatus generally—have not proved satisfactory in the acetic acid industry, simply because they are incapable of withstanding the relatively high temperature of the vapour (118° C.) and it is practically impossible to render them impervious, or at any rate to keep them so.

The prime cost of stoneware columns is less, of course, than that of copper columns. It is by no means unusual, however, to find that at least two stoneware columns or condenser coils have already cracked before the process is in really regular operation; it is then quite obvious that copper columns and silver condensers are cheaper in the long run, especially as regards working costs, since they are absolutely reliable and are very rarely the cause of interruptions in the process.

Similar difficulties are experienced in the use of cast-iron or steel stills lined with earthenware tiles. It is impossible to render this lining quite impervious. The acetic acid works through the joints to the iron shell with the result that hydrogen and hydrocarbons are evolved, which not only impart a perceptible odour to the acetic acid but tend to force the tiles away from the shell.

All attempts up to the present to replace copper by cheaper materials for the construction of acetic acid stills must be regarded as having failed; this remark applies to the substitution of copper by bronze for condenser pipes and steam-coils, in spite of the claims that bronze is more durable.

Well-worked copper is undoubtedly the best material available at present for the construction of acetic acid stills, columns and dephlegmators. For the steam-coils and condensers silver is preferable, though copper proves perfectly satisfactory provided that the presence of traces of metallic impurity in the product is no detriment.

If the object is merely to manufacture acetic acid which shall be free from mineral acid and empyreumatic matter, and suitable for technical purposes, the usual practice is to submit the crude acid, obtained by one or other of the processes mentioned, to simple redistillation in an apparatus such as that shown in Figs. 40 and 43 (pp. 293, 318). The operation is

carried out either under atmospheric pressure or, if waste steam is available, possibly under reduced pressure. Before the distillation is begun, caustic soda or sodium or potassium acetate is added to the charge in sufficient quantity to neutralise the mineral acid present.

The crude acetic acid furnished by the aqueous hydrochloric acid process is nearly always treated in this simple manner; owing to its low concentration (45–50 per cent) it is seldom worked up into glacial acetic acid.

On the other hand, the crude acetic acid which results from the vacuum sulphuric acid process and contains 80 per cent of organic acids is very rarely worked up for technical acetic acid alone; it constitutes the raw material for the manufacture of chemically pure glacial acetic acid (96–100 per cent), which is used both in industry and pharmacy and for the preparation of chemically pure vinegar-essence (80 per cent).

Besides calcium acetate, commercial grey acetate of lime contains calcium propionate and butyrate. The homologous acids derived from these salts pass over into the crude acetic acid and usually constitute about 5 per cent of this product.

In order to purify the crude acid it is necessary :—

1. To separate the water as completely as possible from the acid by distillation, so as to obtain the acetic acid, present in the crude product, in the form of glacial acetic acid (96–100 per cent).
2. To remove the non-volatile organic and inorganic impurities.
3. To eliminate traces of sulphur dioxide.
4. To separate the homologous acids from fractions composed mainly of highly concentrated acetic acid.

The process whereby these requirements are fulfilled consists in the rectification of the crude acid in a column still, which is similar in principle to the intermittent wood-naphtha stills described previously, but is of somewhat different construction, corresponding to the special purpose for which it is designed. An apparatus of this type comprises a boiling-vessel, column, dephlegmator and condenser, as shown in Fig. 42.

Experience has shown that, in order to obtain satisfactory results, boiling-vessels of large capacity—5000 to 15,000 litres—must be employed. These vessels are constructed in the form of cylinders which are disposed either vertically or horizontally.

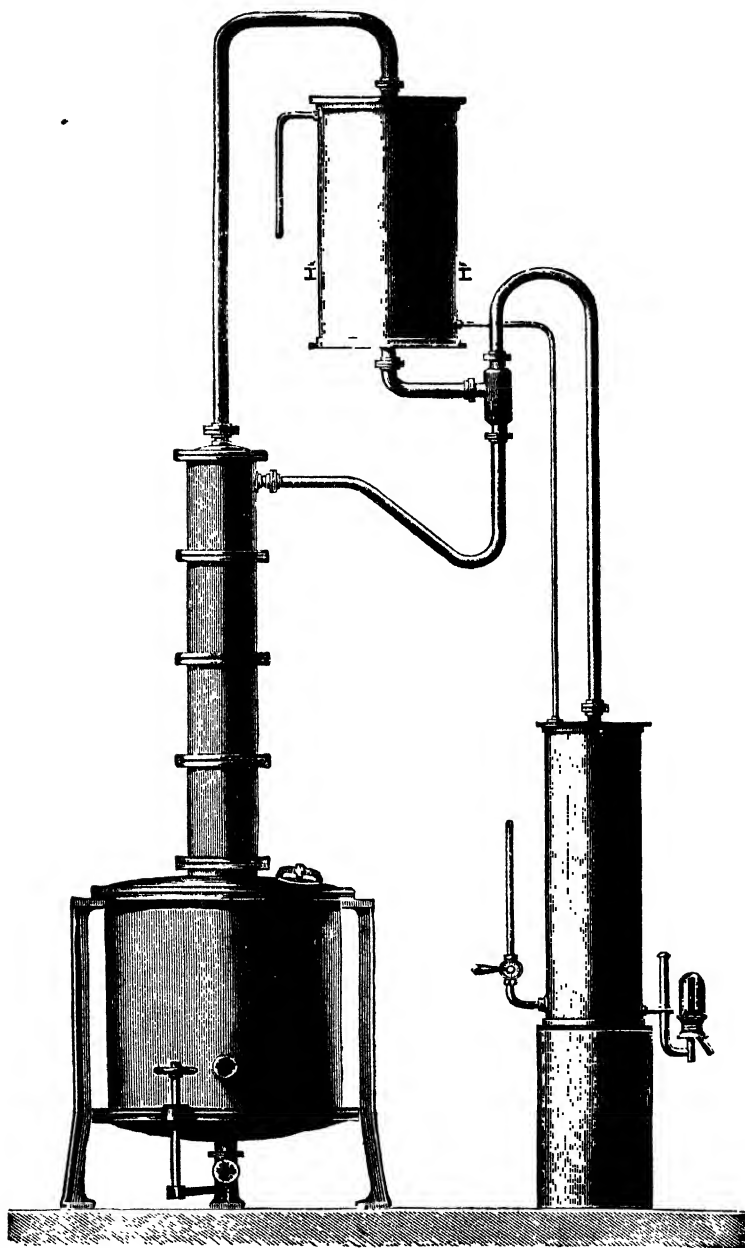


FIG. 42.—COPPER COLUMN STILL FOR THE RECTIFICATION OF CRUDE ACETIC ACID WITH PRODUCTION OF TECHNICAL ACETIC ACID (30-50 PER CENT) AND GLACIAL ACETIC ACID.

It cannot be said that any particular advantage attaches to either position compared with the other. Both the dephlegmator and condenser consist of specially constructed coils of piping.

It is obvious that, in dealing with a product like acetic acid, which exerts an intense solvent action on metal, the question of material becomes unusually important. As a matter of fact very few forms of apparatus have been subjected to such a variety of tests, with a view to finding the most suitable material for construction, as the plant used for the rectification of acetic acid.

The suitability of copper for the purpose has already been mentioned above. In absence of air, copper is capable of offering considerable resistance to the action of organic acids; in that respect, therefore, it is quite satisfactory, but good results can only be obtained provided that the utmost skill is used in the construction of the plant. Owing to the long and intricate joints in the plant and the necessity of providing walls of considerable thickness, it is essential not only that the copper-smith should be thoroughly expert, but also that the workshop in which the plant is constructed should be equipped with all modern appliances for this class of work.

If these conditions are fulfilled, there is absolutely no difficulty in building copper plant which is really durable, and satisfactory in all other respects.

The still is heated by means of a steam-coil made of copper or silver. Formerly, when the plant in general use was of relatively small capacity, steam-jacketed boiling-vessels were usually employed, and even to-day this antiquated method of heating is still frequently to be found. For acetic acid stills this method of heating is unsound. The double bottom is designed, of course, for a definite working pressure, but owing to the action of the acid, the inner shell must necessarily become weaker with continued use; eventually it may be unable to withstand the pressure of the steam and will naturally collapse. If the still is fitted with a column containing porcelain plates, these will probably be shattered and considerable damage may be caused elsewhere.

In modern practice, steam-coils have been adopted almost exclusively for heating purposes. These coils are constructed of drawn piping, and special connections which ensure absolute tightness are used to combine the separate lengths of piping.

For closing the outlet through which the residue is discharged, a cone-plug proves most satisfactory; cocks and valves are unsuitable, since they become unserviceable after a short time owing to corrosion. Apart from the arrangement for discharging the still, and the inlet and outlet connections for the steam pipes, no other fittings should be provided unless absolutely necessary, as they always tend to give rise to leaky joints. The plant should be arranged in such a manner that the bottom of the boiling-vessel can be easily removed without dismantling any other part of the apparatus; in the event of leakage in the steam-coil it is then a simple matter to remove the coil for repair.

The cover of the boiling-vessel is provided with only one manhole, and is fitted at the centre with the neck-piece for connection with the column. The column is composed of a series of cylindrical sections, likewise made of copper and brazed at the seams. The column is fitted internally with perforated porcelain plates, which rest on special copper supports consisting of cylinders open at both ends and arranged concentrically with the shell of the column. The lowest of these supports rests on a copper ring inserted at the base of the column; the first porcelain plate rests on the top of this support; a second copper ring follows, then the second support, and so on, until the necessary number of plates is present. In order to protect the column against corrosion by the acid, the space between the shell and the plate-supports is packed with asbestos. It is quite practicable to use supports and plates made of earthenware, but, as far as the plates are concerned, earthenware is very little cheaper than porcelain; moreover, earthenware plates are rarely made with such accuracy as porcelain plates, consequently, irregularities may easily arise during the course of the rectification.

The column is connected with the dephlegmator which consists of a coil of drawn copper piping. The dimensions of the dephlegmator constitute a factor which exercises great influence on the course of the rectification.

The condenser is similar in construction to the dephlegmator, but of smaller dimensions. If the object of the process is to obtain a distillate free from metallic impurities even at the first rectification, then the still is provided with two condensers, one made of copper and the other of silver, each of which is

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connected by means of suitable fittings directly with the boiling-vessel and also with the dephlegmator.

The first portions of the distillate, which contain sulphur dioxide, are passed through the copper condenser ; as soon as the distillate is free from sulphur dioxide, it is diverted to the silver condenser. The condensers are placed at such a height that the outflowing distillates can be distributed among the various collecting vats, and be run from these directly into glass carboys, wooden barrels, etc., for shipment, or else into the boiling-vessels of other stills for redistillation.

Owing to its nature, acetic acid does not lend itself to transportation by the methods ordinarily adopted for liquids ; hence, in conveying the intermediate and finished products from one place to another inside the factory, the principle of gravitation is utilised to the fullest possible extent.

When the liquid in the still has sunk below the level of the steam-coil, distillation naturally ceases. With properly constructed plant this point is reached when 95-97 per cent of the original charge has been distilled over.

The residue is then a more or less viscous, tarry mass, which still contains 50-60 per cent of volatile acids, reckoned as acetic acid, together with a considerable amount of mineral matter which has been carried over with the distillate during the decomposition of the acetate of lime.

The residue is allowed to remain in the vessel for a short time, and is then removed and distilled separately for the purpose of recovering technical acetic acid.

Starting out with 100 kilos. of crude acetic acid at 80 per cent, the ideal result of the process of rectification would be the production of :—

80 kilos. of acetic acid at 100 per cent.
20 kilos. of water.

Water boils at 100° C., acetic acid at 118° C., and no constant-boiling mixtures are formed ; hence, according to the laws of rectification stated on pages 229-230, the above result might reasonably be expected.

In this case, however, theory and practice do not agree. With aqueous solutions containing less than about 10 per cent of acetic acid, scarcely any separation can be effected by fractional distillation. In dealing with crude acetic acid it is impossible to isolate the water as such, or to obtain

an aqueous fraction containing less than 10-15 per cent of acetic acid; and even this degree of separation can only be effected by an extremely slow process of rectification and the consumption of a large amount of steam.

In the ordinary process of rectification, the water present in the crude acetic acid is usually obtained in the form of a distillate containing 30 per cent of acetic acid.

Leaving out of consideration unavoidable losses, which are only small, it will be obvious that rectification of the crude acid must produce entirely different yields of anhydrous acid (glacial acetic acid) according to the amount of acid which is taken off with the water.

If the rectifying apparatus has been properly designed, it is possible to control, to a certain extent, the amount of acid which passes off with the water; but the limit to which the acid content of the product may be reduced is usually governed by commercial requirements, and the process must be conducted in such a manner that the concentration of the dilute acid satisfies the demands of the consumer.

In Germany the concentration usually required for technical acetic acid is 30 per cent, in America 28 per cent, and in other countries still other concentrations.

The following table demonstrates the influence which the concentration of the "first runnings" exercises on the yield of glacial acetic acid.

Assuming that 100 kilos. of crude acetic acid are distilled in each case, and that the strength of the technical acetic acid varies as shown in the first column, the effect of this variation on the yields—neglecting losses—of technical and glacial acid respectively is clearly shown by the figures in the succeeding columns :—

Strength of technical acetic acid. (First runnings.) Per cent.	Yield of technical acetic acid. (First runnings.) Kilos.	Yield of glacial acetic acid (100 per cent). Kilos.	Yield of glacial acetic acid expressed as percentage of the total content of acetic acid (100 per cent) in the original charge. Per cent.
15	23.50	76.50	95.62
30	28.57	71.40	89.28
45	36.36	63.40	79.25
60	50.00	50.00	62.50

Since glacial acetic acid is usually the most valuable product it follows that the plant in which the process of rectification is carried out must be designed to produce first runnings containing as little acetic acid as possible, and that the process itself must be conducted with the same object in view.

As mentioned above, it is necessary to provide for the separation not only of water but also of the homologous acids and the non-volatile organic and inorganic products which accompany the acetic acid. The non-volatile products remain as the residue in the apparatus, hence their removal offers no difficulty.

It is only necessary, therefore, to consider the elimination of the homologous acids and other volatile organic products which pass over with the acetic acid during the rectification of the crude acid.

Fitz¹ and Hecht² have shown that when a mixture of acetic acid, butyric acid, caproic acid, and water is distilled, the caproic acid always comes over first, followed by the butyric acid and finally by the acetic acid.

A similar phenomenon may be observed during the rectification of crude acetic acid. The water which passes over in the first place carries with it a portion of the homologous acids, so that the first runnings—the technical acetic acid—always contain a certain amount of these acids.

After the whole of the water has been driven over, in the form of a 15–30 per cent solution of acetic acid, the residue in the still consists only of anhydrous acetic acid together with the various impurities which so far have not been distilled off.

At this stage the homologous acids change their rôle, behaving, in the absence of water, no longer as “first runnings” but as “last runnings” in relation to the acetic acid.

Although a certain amount of the homologous acids comes over with the aqueous fraction, the larger proportion remains behind in the tarry residue, and the main bulk of the distillate, constituting the middle runnings, contains little, if any, of these acids.

In practice, rectification of crude acetic acid for glacial acid gives the following products :—

¹ Ber. 1878, **11**, 46.

² Ann. 1881, **200**, 319.

	Per cent (approx.).
1. Turbid first runnings containing SO_2	1.75
2. Water-white dilute first runnings (30 per cent acetic acid)	27.00
3. Water-white glacial acetic acid (98 per cent)	68.25
4. Tarry residue containing about 50–60 per cent of acetic acid and its homologues, reckoned as acetic acid	3.00

Of these fractions, only the water-white technical acid (2) is marketable without further treatment. Instead of selling this product, however, certain factories may prefer to work it up into more highly concentrated acid.

Assuming that the technical acid contains at least 30 per cent of acetic acid, 100 kilos. of this product, by a further process of rectification, should furnish approximately :—

80 kilos. of acetic acid at 15 per cent,
20 kilos. of acetic acid at 90 per cent.

It is seldom possible, however, to find a market for 15 per cent acetic acid, consequently this product must be utilised in some other way. The usual method is to convert it into sodium acetate (p.288), or into acetate of lime for returning to the process.

In deciding whether it is better to sell the 30 per cent acetic acid or to submit it to further treatment, local conditions must necessarily act as the guiding factor.

The glacial acetic acid (3)—96–98.5 per cent CH_3COOH —resulting from the rectification of crude acetic acid is usually unfit for immediate sale, since it contains small traces of copper derived from the condenser, traces of formic acid, and particularly higher-boiling homologues of acetic acid, which lower the degree of purity of the product.

Contamination with metal may be prevented by using silver for the construction of all portions of the apparatus beyond the dephlegmator.

In order to obtain a chemically pure glacial acid (99–100 per cent), or a 96 per cent acid suitable for pharmaceutical purposes, the glacial acetic acid fraction (3) must be submitted to a further process of distillation. This process is carried out in a “fine-acid” still (see Fig. 43) consisting of a copper boiling-

vessel fitted with a silver head-piece which is connected by a silver delivery pipe with a silver condenser.

Before the operation is begun, a small quantity of potassium permanganate is added to the charge of acid in the still, for the purpose of eliminating oxidisable impurities. The distillation is carried out very rapidly and as a rule the only

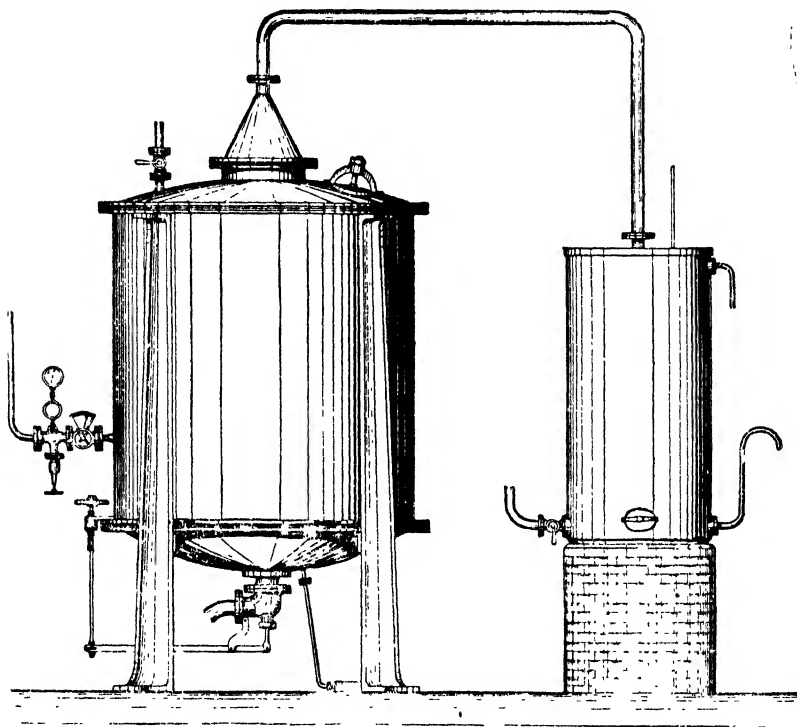


FIG. 43.—“ FINE-ACID ” STILL FOR THE MANUFACTURE OF CHEMICALLY PURE GLACIAL ACETIC ACID (96-100 PER CENT) FROM TECHNICAL GLACIAL ACETIC ACID.

portions of the distillate which must be collected separately are certain amounts of “ first runnings ” and “ last runnings ” which do not reach the standard required for the main product.

The “ middle runnings ” consist entirely of chemically pure glacial acetic acid, which satisfies all the tests prescribed by the different pharmacopœias, and after suitable dilution

smells and tastes pure—an indication of purity which is even more reliable than the behaviour of the product towards permanganate (see p. 401).

This product may then be sold at its original concentration as *chemically pure glacial acetic acid*, or, after dilution to the necessary degree of concentration, as *pharmaceutical acetic acid*; or it may be diluted to 80 per cent and put on the market as *vinegar-essence* for edible purposes. The first and last runnings from the fine-acid plant are returned for rectification with the crude acid.

The remaining product of the rectification of crude acetic acid is the dark-coloured, more or less viscous residue which contains 50–60 per cent of volatile acids, reckoned as acetic acid.

This residue also contains a very considerable amount of mineral matter composed of particles of acetate of lime and calcium sulphate, which have been carried over during the process of decomposition, together with a certain quantity of copper acetate. In order to recover the organic acids, the residue must be distilled in some suitable form of apparatus. In this case the use of indirect steam alone as the heating agent is not sufficient to effect a complete separation of the volatile acids from the remainder of the residue, owing to the high boiling points of certain of these acids.

Distillation over direct fire also gives unsatisfactory results, owing to the presence of the mineral matter in the residue.

Distillation under reduced pressure in steam-heated apparatus is practicable, but certain disadvantages, due to the nature of the residue obtained, attach to this process.

The best method of all consists in heating the residue by means of high-pressure steam, and blowing in direct steam at the same time. As a result, a distillate is obtained which is quite suitable for mixing with technical acetic acid.

This operation completes the treatment of crude acetic acid for the various commercial forms of “pure” acetic acid.

The stills which are employed in the rectification of crude acetic acid are not altogether cheap, chiefly owing to the necessity of using copper plate of very considerable thickness for the construction of the boiling-vessels, which have a capacity of 4–12 cu. metres. For this reason numerous efforts have been made to find a cheaper material which would be

suitable for the construction of the boiling-vessels, but so far without success.

This disadvantage attaching to the *intermittent process* of rectification is no longer present in the *continuous process*, which was introduced by the author. In this process the use of large boiling-vessels is completely avoided.

The principles of a continuous distillation process and the nature of the apparatus employed have already been described in connection with wood-naphtha; it is only necessary, therefore, to deal in outline with the continuous process for the rectification of crude acetic acid.

The course followed by the intermittent process demonstrates that a mixture of water and acetic acid completely obeys the laws which hold good generally for the process of rectification, provided that the water is not present in too large excess.

The continuous acetic acid still consists essentially of a boiling column and a rectifying column, connected as usual with a dephlegmator and condenser.

Suppose that a mixture consisting of 20 per cent of water and 80 per cent of acetic acid is delivered on to the top plate of the boiling column and there meets with an opposing stream of vapour of the same composition; the conditions are then similar to those in the continuous naphtha still and a similar process will operate. The vapour passing from the top plate of the boiling column into the rectifying column will be richer in the lower-boiling component—*water* in this case—than the liquid from which it is derived. The liquid passing down the boiling column becomes continually richer in acetic acid, whereas the vapour passing up the rectifying column becomes continually weaker in acetic acid.

As a result, the whole of the water is gradually extracted from the crude acid entering the apparatus, and the liquid reaching the bottom of the boiling column consists only of glacial acetic acid containing a certain amount of higher-boiling homologous acids and the tarry and mineral impurities.

A certain definite quantity of the glacial acid reaching the bottom of the boiling column is revaporised and supplies the heat necessary for carrying on the process. After the apparatus has been in operation for some time, a state of equilibrium is reached, in the sense that, in a given period, the amounts of water and acetic acid leaving the apparatus in the form of weak acetic acid from the condenser attached to the rectifying

column, and of glacial acid from the bottom portion of the boiling column, are equal to the amounts of water and acetic acid entering the apparatus.

The vapour passing upwards through the rectifying column becomes gradually weaker in acetic acid, and finally leaves the condenser in the form of liquid containing 20–25 per cent of acid.

The glacial acid obtained in this manner still contains all the components which constitute the “residue” of the intermittent process, namely, the higher homologues of acetic acid and the tarry and mineral impurities.

The product must therefore undergo purification, for which purpose it is taken off at a definite rate from the bottom of the boiling column through a pipe which conveys it to a third column; in this the glacial acid is separated from the homologous acid and the solid impurities on exactly the same principle as governs the process in the first and second columns.

An apparatus of this type includes only one vessel, namely, the chamber at the base of the boiling column, which need only be large enough to contain the closed steam-coil used for heating the apparatus.

A further advantage is that the internal metal surfaces are never brought into contact *alternately* with acetic acid vapour, liquid acetic acid and air, as in the intermittent apparatus. In the intermittent process air naturally enters the plant during the operations of charging and discharging, and tends to oxidise the copper surfaces which are moistened with acetic acid. The oxide is dissolved during the next distillation, and as a result of this action the costly intermittent apparatus is worn out more rapidly than the cheaper continuous apparatus into which air seldom enters.

The continuous apparatus is particularly efficient; it requires less attention and consumes less steam than the intermittent apparatus; at the same time it is only suitable for factories which carry out the manufacture of acetic acid on a relatively large scale.

II. MANUFACTURE OF ACETONE

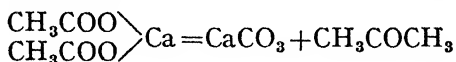
Apart from its use for the manufacture of acetic acid, acetate of lime is also employed in large quantities for the production of acetone.

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At one time this product found practically no application except for scientific purposes, but during the last twenty-five years it has been introduced into the arts to an important extent. The celluloid industry makes use of acetone for gelatinising nitrocellulose, and an even greater and steadily increasing amount is consumed by the smokeless powder factories. Great Britain, in particular, requires considerable quantities of acetone for use in the manufacture of cordite, and formerly a large proportion of the acetone produced in Germany was exported to England for that purpose, though the British Government also carried on the manufacture of acetone to a certain extent.

Acetone also serves for the manufacture of ionone, iodoform and chloroform, for the absorption of acetylene and for many other purposes. Certain by-products of the manufacture of acetone—the so-called acetone oils—are used in the preparation of denaturants or serve directly for denaturing industrial alcohol. Hence, at the present day, acetone has become an article of considerable commercial importance.

During the past few years, processes of manufacturing acetone have been developed in which the raw materials employed are other than the products of the wood-distillation factories. It may be claimed, however, that the most important industrial process is still the *destructive distillation of acetate of lime*, whereby this product is converted into acetone and calcium carbonate, according to the following equation:—



which, in principle, applies generally to the formation of ketones from the salts of fatty acids.

When acetate of lime is subjected to destructive distillation the organic impurities, and especially the calcium salts of the higher acids accompanying the calcium acetate, likewise undergo decomposition. At the temperature necessary for effecting the decomposition of acetate of lime—about 400° C.—the organic impurities become coked, with the formation of tar-oils and gas. The free lime, which is usually present in the acetate owing to the practice of “overliming” to a certain extent during the process of neutralising the pyroligneous acid (see p. 202), reacts with the calcium salts of the organic acids to form hydrocarbons and calcium carbonate. This

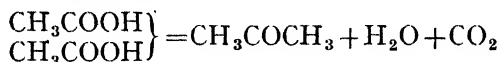
reaction is similar to that which takes place when the salts of fatty acids are heated with caustic alkalis for the preparation of hydrocarbons; it may be represented generally by the equation :— $\text{CH}_3\text{COONa} + \text{NaOH} = \text{Na}_2\text{CO}_3 + \text{CH}_4$

The calcium salts of the higher fatty acids undergo decomposition, in exactly the same way as calcium acetate, to form higher ketones. Apart from these primary products of destructive distillation, certain secondary products are also formed in the course of the process, partly owing to local overheating, partly by the decomposition of primary products as a result of passing over strongly heated metal surfaces. All these factors exercise an important influence on the process, hence it is scarcely surprising that the theoretical yield of acetone is not attained in practice.

Theoretically, the maximum amount of acetone which can be obtained from 100 kilos. of grey acetate of lime (80–82 per cent) is about 30 kilos., provided that the above weight of grey acetate does actually contain 80 kilos. of calcium acetate. In dealing with the manufacture of acetic acid, however, it has been shown that grey acetate of lime contains at least 5 per cent of the calcium salts of higher fatty acids. On destructive distillation, these salts produce higher ketones, which appear as by-products—the so-called acetone oils—during the purification of crude acetone. In spite of the utmost precaution in carrying out the preliminary distillation, the use of superheated steam as a heating agent, and the exercise of the greatest care in conducting the process of rectification, it has been found impossible, so far, to produce much more than 20.2 kilos. of pure acetone from 100 kilos. of acetate of lime, at any rate of such quality as to satisfy the stringent requirements of the manufacturers of smokeless powder. Higher yields are frequently claimed, but usually these may be explained by the fact that a portion of the methyl ethyl ketone, which can be isolated in a very pure state from the acetone oils, has been mixed with the pure acetone. This is permissible as long as the product is intended for use in the manufacture of celluloid, or for other industries in which the consumers of acetone are less strict in their requirements than the manufacturers of smokeless powder.

Apart from the destructive distillation of acetate of lime, only one other process for the manufacture of acetone is really

closely associated with the wood-distillation industry, in that it starts out from acetic acid. This process, which was worked out in the first place by Schiff¹, consists in passing dilute acetic acid vapour over pumice impregnated with barium acetate, magnesium acetate, or any other acetate which will act in a similar manner; in this way a large surface of the salt is exposed. The pumice is contained in tubes, which are heated externally to the temperature at which the reaction resulting in the formation of acetone takes place. As soon as the mixture of acetic acid and water vapour comes into contact with the barium acetate, or barium oxide formed by the decomposition of the acetate, the acetic acid is converted directly into acetone and carbon dioxide, according to the equation:—



Unfortunately, this reaction, which appears to offer the possibility of manufacturing acetone by a continuous process, never proceeds as smoothly as the above remarks may suggest. In the first place, no matter whether the concentration of the acetic acid is high or low, the reaction is never quantitative, as is clearly demonstrated by the evolution of gas (ethane) and the presence of free acetic acid in the distillate.

Any process which rendered possible the manufacture of acetone directly from pyroligneous acid vapour after removing the wood-naphtha would offer a distinct advantage over the acetate of lime process, assuming that it produced an equal yield. It would no longer be necessary to convert the pyroligneous acid into acetate of lime, and it would be possible, therefore, to avoid the costs of supplying lime and evaporating the acetate liquor.

A simple calculation will give us the amount of these costs. Theoretically 100 kilos. of acetate of lime (80–82 per cent) require 28.5 kilos. of quicklime at 100 per cent CaO, or about 30 kilos. at 95 per cent CaO. Assuming that 5 per cent excess of lime is used, 100 kilos. of acetate of lime (80–82 per cent) require 31.5 kilos. of lime (95 per cent CaO). If the price of lime is 1.5s. per 100 kilos. this represents a cost of 0.47s. The strength of the acetate solution is about 25 per cent. Consequently, 300 kilos. of water must be evaporated

¹ Wagner's "Chem. Technologie," 1895, p. 515. British patents 2816/1898 and 15,907/1898; German patent 114,196.

for every 100 kilos. of finished acetate produced, for which purpose $300 \times 1.20 = 360$ kilos. of steam, or $\frac{360}{7.5} = 48$ kilos. of coal, are required. Assuming that the price of coal is 20s. per 1000 kilos. this represents a cost of 0.96s.

The total saving per 100 kilos. of acetate of lime (80–82 per cent) amounts, therefore, to $0.47 + 0.96 = 1.43$ s. By taking into account the saving effected in respect of wages and depreciation charges also, this figure becomes increased to about 1.75s.

Certain trials which were carried out on the direct process showed that out of 500 kilos. of vaporised 10 per cent acetic acid (=50 kilos. of absolute acid) a proportion equivalent to no less than 30.9 kilos. of absolute acid passed over into the distillate with the acetone. In addition 9.4 kilos. of absolute acid remained in the residue in the still. Hence, out of 50 kilos. of acetic acid (100 per cent), employed in the form of a 10 per cent aqueous solution, only 9.7 kilos. or about 19.4 per cent underwent conversion. Moreover, the acid was not converted into acetone alone, since the total yield of that product amounted to only 2.7 kilos. contained in a total distillate of 427 kilos.

In order to recover the acetone it would be necessary, therefore, to submit 427 kilos. of distillate—containing about 7.2 per cent of acetic acid and only 0.63 per cent of acetone—to fractional distillation, and to return the residue containing acetic acid to the process or else to convert it into brown acetate of lime, since it would scarcely be suitable for the manufacture of any other product.

Assuming that the former and simpler of the two methods of disposal is adopted, namely, the return of the weak acetic acid to the process, then, for every 2.7 kilos. of acetone produced, at least 400 kilos. of water must again be vaporised, or for 20 kilos. of acetone—the yield obtainable in practice from 100 kilos. of acetate of lime—2962 kilos. of water must be vaporised. This operation requires $\frac{2962}{7.5} = \text{approx. } 400$ kilos. of coal, at a cost of 8s.

We have seen above that the saving in the direct process, compared with the acetate of lime process, amounts to 1.75s. or in round figures 2s. per 20 kilos. of acetone produced.

Against this saving of 2s. we have therefore to set an expenditure of at least 8s. for the cost of vaporising the weak acetic acid which, in consequence of the low degree of conversion, must be returned repeatedly to the process.

In view of these figures it would appear impossible for the direct process to compete with the acetate of lime process unless the former were capable of producing correspondingly higher yields.

According to the report on the above-mentioned trials 9.7 kilos. of absolute acetic acid produced on conversion a total of 2.7 kilos. of acetone. This product, however, was not pure acetone, as it still contained the homologous ketones which are always produced at the same time.

Theoretically, 9.7 kilos. of absolute acetic acid should produce 4.68 kilos. of acetone, hence the direct process furnishes only about 58 per cent of the theoretical yield, and even this amount includes the higher ketones.

We must now compare this yield with that obtainable by the acetate of lime process.

In practice it has been shown that many factories are capable of producing with certainty 20 kilos. of chemically pure acetone (quite apart from the acetone oils) from 100 kilos. of grey acetate of lime (82 per cent).

100 kilos. of grey acetate (82 per cent) are equivalent to 61–62 kilos. of acetic acid, which will produce 20 kilos. of chemically pure acetone or 25 kilos. of total ketones.

The theoretical yield of ketones from 61–62 kilos. of acetic acid amounts to about 30 kilos., hence the yield from the acetate of lime process is about 83.3 per cent of the theoretical, compared with only 58 per cent for the direct process.

A relatively low yield of acetone, high working costs and various other factors all tend to operate against the adoption of the direct process into actual practice.

In short, the process can scarcely be regarded as present as really practicable.¹

Destructive Distillation of Acetate of Lime.—When acetate of lime is subjected to destructive distillation, formation of acetone sets in to a slight extent at temperatures between 150° and 200° C., but complete decomposition can only be effected by exposing the mass to a temperature of about 400° C. If a moderately large quantity of acetate of lime is distilled as one

¹ See chap. xxi.

charge, it is somewhat difficult to heat the material uniformly, since the latter is a bad conductor of heat and special care must be taken to avoid overheating the surfaces on which it rests.

In these conditions, therefore, it is essential that the acetate should be stirred continuously during the process of destructive distillation, but many disadvantages attach to the process when it is carried out on these lines.

Constant stirring produces a large amount of dust, which finds its way into the delivery pipes and condenser; consequently, these portions of the plant become choked and require frequent cleaning. The dust also contaminates the distillate. Stirring also reduces the residue of the process to a fine powder; on being discharged, this residue produces clouds of dust, which have an injurious effect on the operators and gradually cover the interior of the buildings and the surroundings of the factory generally with a thick deposit. Moreover, the stirring apparatus requires considerable power and tends to break easily.

In spite of these facts, nearly every acetone factory employed this form of apparatus up to a few years ago.

The details and arrangement of this apparatus are clearly shown in Fig. 44. It consists essentially of a shallow cast-iron pan, set in brickwork and heated by direct fire. A cast-iron cover, which is bolted on to the dish, carries the driving gear for the stirrer, and is provided with a manhole and a short outlet pipe to which a vertical dust-trap is attached. The dust-trap is connected with the condenser by means of a delivery pipe. A steam pipe for conveying steam to the interior of the vessel also passes through the cover. The pan is provided with an outlet at the bottom for the purpose of discharging the residue. The condenser is fitted with a gas-separator which delivers the non-condensable products of the process through a pipe into the chimney or simply into the open air.

As a rule, the charge of acetate varies from 120 to 300 kilos. It will be obvious from the nature of the process that the layer of acetate must not be too thick and that the stirring apparatus must operate efficiently, since it is essential that the individual particles of acetate of lime should be moved uniformly and repeatedly over the strongly heated surface of the pan; otherwise the acetate will tend to burn, and form a scale on the bottom of the pan.

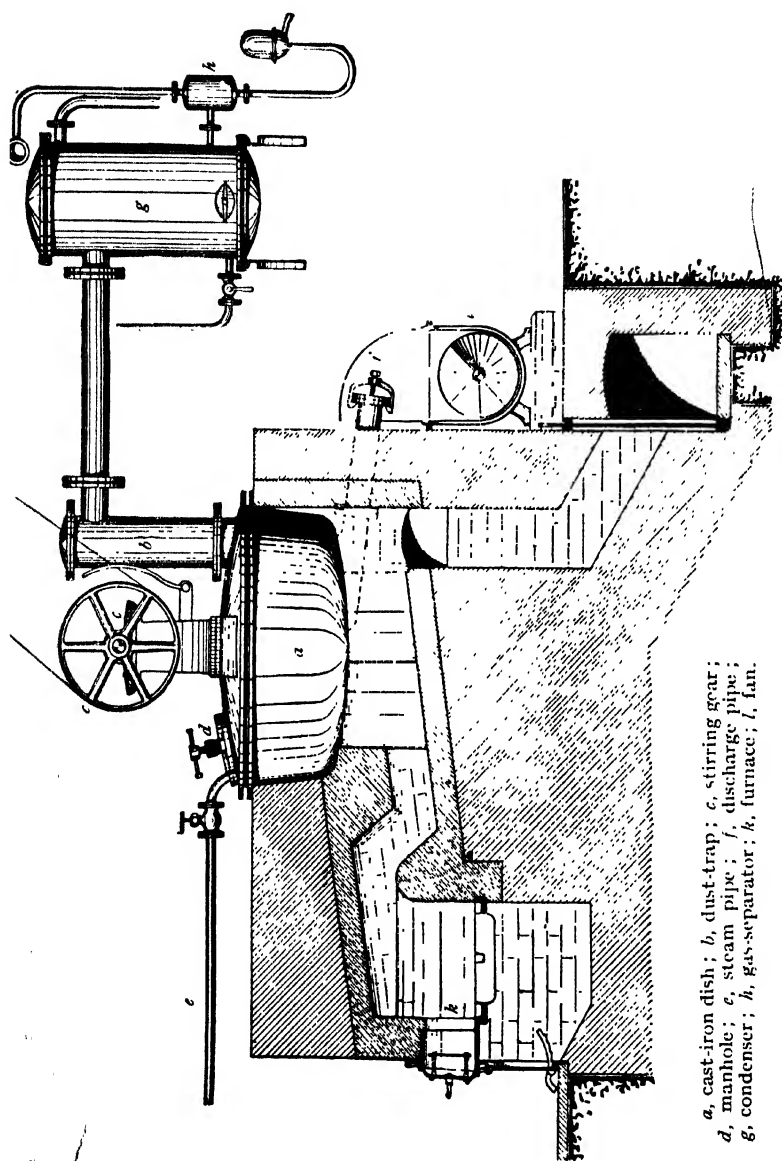


FIG. 44.—APPARATUS FOR THE MANUFACTURE OF CRUDE ACETONE BY THE DESTRUCTIVE DISTILLATION OF ACETATE OF LIME.

a, cast-iron dish; *b*, dust-trap; *c*, stirring gear;
d, manhole; *e*, steam pipe; *f*, discharge pipe;
g, condenser; *h*, gas-separator; *k*, furnace; *l*, fan.

The troubles arising from the formation of dust have already been mentioned above. Lack of supervision during the process, badly designed plant, or failure to keep the apparatus clean, may easily lead to choking, which, in view of the highly inflammable nature of the product, may have very serious consequences.

In order to avoid these difficulties as far as possible, a dust-trap is placed between the vessel and the condenser. These dust-traps must be very considerably larger than those used in the acetic acid process.

This type of acetone plant is heated exclusively by direct fire. In the early days of the process it was a common practice to surround the pan with an outer vessel containing molten lead, the object being to supply heat uniformly to the apparatus at constant temperature. The use of a lead bath, however, has never proved satisfactory in any process, since the molten lead, in the presence of the air which naturally finds its way into the bath, becomes converted gradually into lead oxide, and eventually the contents of the vessel become completely solid.

In consequence, the risk of overheating is just as great as when direct fire is employed, and the fuel consumption is largely increased. For these reasons the use of lead baths has been abandoned, and direct-fired pans are now employed exclusively in those factories which still operate the type of acetone plant described above.

In this process particular importance attaches to the design of the furnace. If the furnace is unsuitably constructed, fine-pointed flames may impinge on the cast-iron dish and eventually cause it to crack.

Uniform heating is of the highest importance and is attained best of all by leaving considerable space between the actual fire and the bottom of the pan (see Fig. 44).

In this way it is possible to ensure that flames will not reach the pan and that hot furnace-gases alone will act as the heating agent.

In working the process, the cast-iron pan is heated gradually to about 400° C. This operation must be carried out slowly and regularly in order to prevent cracking of the brickwork. As soon as the pan exhibits a dull cherry-red glow, the charge of acetate of lime is introduced. In small factories the material is usually emptied directly from

the sacks into the apparatus, thus causing all manner of inconvenience owing to the dust. In large factories, however, it is usual to store the acetate in a room immediately above the acetone plant. While the plant is in operation, the acetate intended for the next charge is filled into a movable wooden hopper which is closed at the bottom by means of a wooden slide. When the plant below has been emptied and is ready for a fresh charge, the hopper is run over a charging hopper in the floor, which delivers the acetate directly through the open manhole of the acetone plant below.

The manhole cover is then replaced and luted down with clay, and the stirrer is set in motion. After a short time, white fumes appear at the end of the pipe leading from the gas-separator—an indication that the process has already begun. This "*blow*" ceases as soon as the distillate begins to flow from the condenser. The distillate consists at first chiefly of the water which is present in the acetate to the extent of about 10 per cent. As mentioned above, this water is only expelled from the acetate at temperatures above 150° C. The aqueous distillate, known as "*acetone water*," shows an average specific gravity of 1.01–1.02, the relatively high value being due to particles of acetate of lime which have been carried over by the vapour and have dissolved in the condensed liquid. The average acetone content of the aqueous distillate, as derived from the results of a large number of analyses, is about 3 per cent, but owing to the fact that the estimation in each case was carried out by the Messinger method (see Analytical Section, p. 422), this figure also includes all other substances present which are capable of producing iodoform on titration with a solution of iodine.

After the water has been driven over, distillation ceases and during this period firing must be carried on vigorously. This pause lasts for about 10–15 minutes, after which crude acetone begins to distil over, the rate of flow usually being considerably greater than during the previous period. The aqueous distillate is mostly pale yellow, but the product during the actual acetone period is more or less dark brown and possesses an intensely characteristic odour. After a certain time the rate of flow diminishes steadily, and finally the distillate comes over in drops. Towards the end of this period the delivery pipes are already beginning to cool—an indication that very little vapour is now

passing over and that the process is completed. If at this stage the apparatus were opened up, the acetone vapour still present in the vessel would certainly become ignited as a result of the influx of air. In the first place, therefore, it is necessary to drive out the vapour which remains in the apparatus by blowing in steam. This operation not only prevents the danger of fire but also ensures recovery of the last traces of acetone from the apparatus : hence, for reasons both of safety and profit, it should never be neglected.

Afterwards the apparatus may be opened without further hesitation and the residue removed. This residue consists of a grey powder which has been reduced to a very finely divided, dusty condition by the action of the stirring apparatus ; in the hot state it still possesses an empyreumatic odour. The method usually adopted for removing the residue is simply to shovel it out through the open manhole. This is a very disagreeable operation, however, since the hot dust affects the workmen and covers everything in the neighbourhood of the apparatus.

This objection has been overcome to a large extent by employing suction-fans. In this way it is possible to remove the more finely divided and dusty portions, but the coarser particles remain behind and it is still necessary to use a shovel in order to empty the vessel completely. Nowadays the vessels are provided with an outlet pipe at the bottom for discharging the residue (see Fig. 44), as in the acetic acid plant, and this method has undoubtedly proved more satisfactory.

The pits in which the residue is deposited should be well covered up, otherwise even a light wind will throw up very objectionable clouds of dust from the finely divided mass.

The distillate from each individual condenser belonging to the acetone plant flows into a collecting pipe, which is common to all the condensers and conveys the crude acetone to a collecting tank.

The condensers employed in this process require to be cleaned at frequent intervals in order to remove the deposit of acetate dust which is always carried over by the vapour in spite of the use of a dust-trap. The best form of condenser for the purpose consists of a series of straight tubes connected together outside the water-tank by means of bends ; it has already been described in connection with the condensation of

pyroligneous acid (see Fig. 18, p. 185). If a condenser of this type becomes choked, it is a simple matter, after removing the bends, to clean out the tubes with a brush or other suitable instrument.

Distillation of 100 kilos. of acetate of lime (80–82 per cent) by this process, followed by treatment of the crude acetone, produces at the most 18 kilos. of chemically pure acetone (99 per cent). At one time this yield was considered quite satisfactory, but nowadays it is looked upon as inferior.

The numerous disadvantages attaching to the use of fire-heated pans fitted with stirring apparatus provided obvious reasons for the attempts which were made to find some other method of carrying out the destructive distillation of acetate of lime, especially a method which would no longer involve the necessity of stirring the material.

In the plant described above, heat is transmitted *indirectly* to the acetate, which is kept in motion, whereas the source of heat is in a state of rest. In these conditions, overheating and possibly secondary decomposition may easily take place, however efficiently the material is stirred.

The conditions would be quite different, however, if the heating were carried out by bringing some suitable gas, which had been heated previously to the necessary temperature, into direct contact with the acetate of lime.

“Burning” would then be impossible since the temperature of the heating agent could be carefully controlled; moreover, during its passage through the apparatus, the heating agent could be brought into contact with every single particle of acetate of lime. In contrast to the previous process, the heating agent would in this case be in motion and the acetate of lime at rest.

For this purpose, however, a true gas is quite unsuitable, since it would become saturated with acetone, which could never be recovered completely from the gas; in fact, partial recovery would be a matter of considerable difficulty.

The heating agent best suited to this particular form of the acetone process is undoubtedly *superheated steam*. In its properties this agent closely resembles a gas, and its temperature can be regulated at will, but in contrast to a true gas it offers the great advantage that, after performing its function in the apparatus, it can be condensed completely; at the same time

the acetone with which the steam is saturated also condenses and is therefore recoverable quantitatively.

In practice this process offers several important advantages. Owing to the absence of stirring apparatus much less dust is formed during the actual operation of the plant; in consequence, the residue is less dusty, and discharging is no longer such a disagreeable operation. Choking of the delivery pipes and condensers is very considerably reduced, though it cannot be prevented entirely since the current of steam carries with it a certain amount of acetate. The cost of power for driving the stirring apparatus is eliminated, and the durability of the plant is quite satisfactory.

Most important of all, however, is the excellent yield of acetone which can be obtained by this process, owing to the possibility of heating the charge uniformly and controlling the temperature of the heating agent without difficulty, thus preventing overheating at any point in the apparatus. The yield amounts to 20–20.5 kilos. of chemically pure acetone per 100 kilos. of grey acetate of lime (80–82 per cent).

The most serious drawback in connection with the process is the relatively large amount of superheated steam which must be passed through the apparatus in order to ensure complete decomposition of a given quantity of acetate of lime.

The crude acetone resulting from the process contains only about 3 per cent of acetone; that is, for every kilo. of acetone (=5 kilos. of acetate of lime) about 33 kilos. of steam must be passed through the apparatus. (The water present in the acetate comes over at the same time, but amounts to only 0.5 kilo.)

Hence, a daily production of 100 kilos. of acetone (=500 kilos. of acetate) involves the consumption of 3300 kilos. of steam, equivalent to 450 kilos. of high-class coal. In addition, coal is required for superheating the steam and heating the apparatus externally, the amount according to practical experience being about 300 kilos. per 100 kilos. of acetone produced. The total consumption of coal is therefore 750 kilos.

According to this figure 100 kilos. of acetate of lime will require 150 kilos. of high-class coal, which represents an enormous expenditure in fuel, quite out of proportion to the slightly increased yield—about 0.5 kilo.—which this process is capable of giving. The cost of 150 kilos. of fuel will always be greater than the value of 0.5 kilo. of acetone and thus the

advantage represented by a slight increase in yield is more than neutralised.

A further disadvantage attaching to this process is the necessity of utilising only acetate which is free from dust and has therefore been screened previously.

For this reason, the process is only applicable when some use can be found for the acetate dust which is separated by the screens, as, for example, in factories which manufacture both acetone and acetic acid.

Rectification of the crude distillate requires a relatively high expenditure of fuel, owing to the fact that the crude product contains only 3 per cent of acetone.

The superheated steam process is carried out in vertical iron retorts which are oval in cross-section and are provided with an upper opening for charging and a lower opening for discharging. The charge of acetate is about equal to that used in the stirrer plant.

A dust-trap is installed between the retort and the condenser.

Apart from the openings for charging and discharging, the whole of the retort is enclosed in a brickwork setting which allows the furnace gases from a steam superheater, situated directly adjacent, to circulate around the retort.

The steam superheater consists of the usual tube system, composed of Perkin tubes heated by direct fire.

The superheated steam enters the retort at the bottom and passes upwards, thus coming into thorough contact with the acetate and supplying the amount of heat necessary to effect decomposition.

At the same time the flue gases from the superheater furnace circulate round the outside of the retort and then pass into the chimney.

Distillation is continued until a sample of the distillate—tested by Messinger's method—shows a sufficiently low content of acetone.

The total ketone content of the distillate, as determined by Messinger's method, rarely amounts to more than 3 per cent; hence, the destructive distillation of 100 kilos. of grey acetate by this process produces about 750 kilos. of distillate.

As mentioned above, the enormous consumption of steam neutralises the very considerable advantages attaching to this process. For this reason the author attempted to find some practicable method of converting acetate of lime into acetone

by destructive distillation which would not involve the use of stirring apparatus or superheated steam.

This object was achieved by the invention of the process specified in the German patent 134,977, which provides for the treatment of acetate of lime in shallow layers.

This process is carried out by spreading the acetate in layers, 2-4 cm. thick, on metal trays or perforated plates; the latter are then introduced into a muffle or retort which has been heated previously to the required temperature by some external source of heat.

Decomposition takes place just as completely as in the stirrer plant, but practically no dust is formed since both acetate and heating agent are at rest; burning is impossible since the acetate of lime never lies on directly heated metal surfaces; the distillate is obtained in concentrated form, and the amount of coal required for the decomposition of 100 kilos. of acetate is only 50 kilos., compared with 150 kilos. for the superheated steam process.

Moreover, the yield of acetone from this process is only very slightly inferior to that from the superheated steam process.

The average yields from a number of factories which operate this process are: 20.03 kilos. of chemically pure acetone (99 per cent) stable to permanganate, 2.5 kilos. of white acetone oils (methyl ethyl ketone) and about 3 kilos. of yellow acetone oils per 100 kilos. of acetate of lime (80-82 per cent).

On comparing this process with the others, its advantages are obvious. The above figures show that the yield of acetone is superior to that from the stirrer plant (18 kilos. of acetone per 100 kilos. of acetate) and very nearly equal to that from the superheated steam process (20.5 kilos. of acetone per 100 kilos. of acetate); moreover, the amount of fuel consumed is much less than in the latter process. Absolutely no dust is formed during the operation of the plant, and it is unnecessary to use either screened or granulated acetate.

On the industrial scale, the process is carried out by spreading the acetate on sheet-iron trays which are arranged in tiers on movable racks or cars (see Fig. 45), sufficient space being left between the trays to allow of the escape of the gases and vapours.

The cars are run into horizontal retorts, the floors of which are level with the ground, and the retort doors are then closed.

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Each retort treats about 2000 kilos of acetate of lime in twenty-four hours and is heated directly from a furnace. The firing may be regulated in such a manner that the retort is uniformly heated along its entire length and no part of the shell is in danger of being rendered incandescent by the action of fine-pointed flames.

The retort is connected directly with the condenser, which may be of simple construction since no dust passes into it; a dust-trap is therefore unnecessary.

The same chemical processes take place in the retort as in

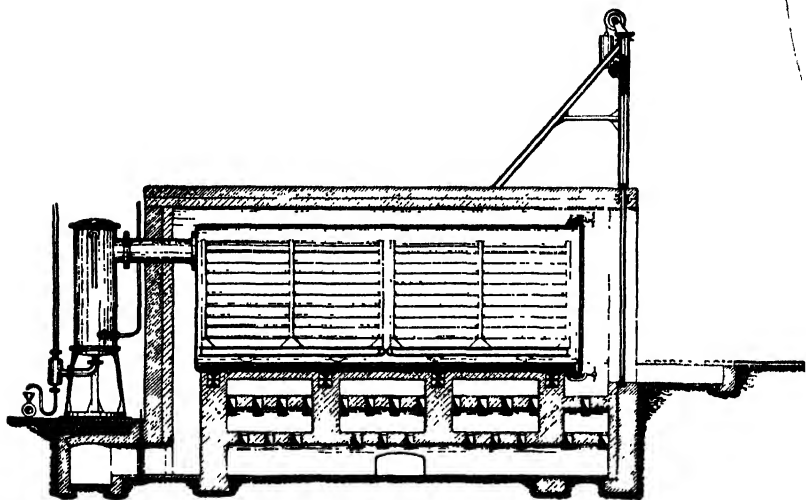


FIG. 45.—APPARATUS FOR THE MANUFACTURE OF ACETONE BY THE DESTRUCTIVE DISTILLATION OF ACETATE OF LIME IN SHALLOW LAYERS.¹

the stirrer plant; in the former case, however, both the acetate of lime as well as the source of heat are completely at rest, since transmission of heat takes place by radiation from the walls of the retort.

The external phenomena of the retort process are also similar to those of the stirrer process; here again, the last traces of acetone are removed by passing in steam before opening the retort.

When the distillate is free from acetone, the retort door is opened, the cars are withdrawn and are replaced immediately

¹ German patent 134,977.

by fresh cars charged with acetate of lime ; hence, the process is nearly continuous.

Charging and discharging of the retort are carried out with ease, and are unaccompanied by the slightest evolution of dust.

Treatment of Crude Acetone.—The crude acetone, no matter by which of the above processes it has been produced, contains all the condensable products resulting from the decomposition of acetate of lime.

Acetone is derived from the actual calcium acetate. The homologous calcium salts (calcium propionate, butyrate, caproate) give rise to higher ketones and—as a result of interaction with calcium acetate—to mixed ketones, especially methyl ethyl ketone.

The destructive distillation of calcium formate alone and in the presence of the above-mentioned calcium salts results in the formation of aldehydes (formaldehyde, acetaldehyde). Finally, from the remaining organic matter present in grey acetate of lime a large number of volatile decomposition products is formed.

Since the above-mentioned main reactions are always accompanied by secondary reactions, the products of which are partly gaseous, it will be obvious that crude acetone represents anything but an individual compound, and the appearance of non-condensable gas and volatile acids during the destructive distillation of acetate of lime can readily be explained. Crude acetone, if not too dilute, forms a brownish black liquid possessing a characteristic odour and varying in specific gravity according to the quantity of "blow-out water" present.

If the apparatus has been blown out with only a small amount of steam at the end of the process, the product is a homogeneous liquid. Otherwise the crude acetone separates, on standing, into two layers, the lower of which is light-coloured and contains the main bulk of the acetone, whereas the upper layer is dark-coloured and consists of those components—higher ketones, hydrocarbons, etc.—which are insoluble or sparingly soluble in water.

Crude acetone usually shows an acid reaction owing to the presence of volatile acids.

The following table gives the approximate yields of crude acetone which may be expected from 100 kilos. of absolute

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acetic acid when the latter is subjected to decomposition by the different processes; also the yields of chemically pure acetone obtained in practice:—

Process.	Yield of <i>crude acetone</i> from 100 kilos. of absolute acetic acid.	Yield of <i>chemically pure acetone</i> from 100 kilos. of absolute acetic acid.
	Kilos.	Kilos.
1. Direct conversion of acetic acid into acetone	4400	26
2. Destructive distillation of acetate of lime in stirrer plant	80	29
3. Destructive distillation of acetate of lime by means of superheated steam	1250	33
4. Destructive distillation of acetate of lime by the author's process ¹ .	80	33

This table shows at once that the amounts of crude acetone obtained from processes 1 and 3 are enormously greater than those from processes 2 and 4; consequently the amount of fuel required in those cases for the rectification of the crude acetone must also be greater.

Crude acetone cannot be utilised directly in any of these forms, since only the chemically pure product may be employed for the manufacture of smokeless powder, and the requirements for the celluloid industry are only a little less stringent.

Crude acetone must be refined, that is, the pure acetone must be isolated from the acids, aldehydes, ketones, hydrocarbons and tarry matter present in the crude product.

Here again, this object is achieved mainly by rectification, but certain of the components are eliminated by chemical means, for example, the volatile acids and aldehydes, which are neutralised or resinified by treating the crude product with alkalis. The insoluble ketones, hydrocarbons, etc., are separated from the acetone by washing with water, in which acetone is soluble in all proportions.

The crude acetone from processes 1 and 3 (see above table), after addition of excess of alkali or alkaline earths and separation of any oil floating on the surface, may be rectified directly without further treatment.

On the other hand, the much more highly concentrated

¹ German patent 134,977.

crude acetone from processes 2 and 4 must be diluted to such a degree that the insoluble ketones, etc., separate out as completely as possible and float on the surface of the liquor. For this purpose the addition of an equal volume of water to the crude acetone is usually sufficient, the operation being best carried out in a closed tank fitted with stirring apparatus.

The stirring apparatus is started up, the liquor vigorously mixed for some time, and the contents of the tank are then allowed to stand. The liquor separates into two layers, the lower consisting of an aqueous solution of acetone, and the upper of the main bulk of the acetone oils present in the crude acetone. At the same time these oils take up the main bulk of the tarry matter; in consequence the upper layer is more darkly coloured than the acetone solution below. The latter is run into a tank which holds sufficient liquor to form one charge for the still. The oils are run into another tank in which they are allowed to accumulate until a sufficient quantity for further treatment—namely, distillation in a current of steam—has been obtained.

For the manufacture of *pure acetone* from an aqueous solution of any concentration, the latter, after being treated as described above, is submitted to fractional distillation in a column still similar to that used for the rectification of wood-naphtha. In practice, it is usual to work with the largest possible charges, as much as 20–30 cubic metres being treated at once in the first distillation.

The first portion of the distillate is always coloured, since it contains in solution the oils which remained in the apparatus after the last fractions had been driven over in the previous operation. This first fraction—or “first runnings”—also contains aldehydes, amines and other impurities, and indicates about 96 per cent on the Tralles alcoholometer. Then follow fractions which already possess the characteristic odour of pure acetone and show a content of about 99 per cent. These fractions become turbid on dilution with water, but the succeeding portion of the distillate is miscible with water in all proportions. The miscible fractions are tested for stability to permanganate solution, and those portions which satisfy the test (see p. 395) are removed from the process as the finished product. All portions of the distillate which do not withstand the test must undergo a second rectification.

The first distillation produces only a small percentage of acetone which satisfies the permanganate test. The beginning of the final stage of the operation is indicated by the spirit hydrometer at the outlet of the condenser gradually rising in the liquor and showing a fall in the concentration from 99 to 98 per cent, and so on. This portion of the distillate is collected as one fraction, as long as a sample on treatment with water is only rendered turbid and no globules of oil separate out on the surface.

The next portion of the distillate is colourless; but when it is treated with water, oils separate out on the surface. Finally a stage is reached at which the distillate is so weak in acetone that the oils are no longer held in solution, and the liquid issuing from the condenser is already separated into oils and water. The oils gradually diminish in quantity until finally the distillate is almost free from oil and consists only of cloudy empyreumatic water. The operation is then complete and the residue in the still may be run off.

The fractions from which oils separate out directly on addition of water are run into a washer, consisting of a horizontal cylinder fitted with stirring apparatus; here they are diluted with water until no further separation of oils takes place. The lower aqueous layer is usually employed for diluting the crude acetone. The last portions of the distillate, which contain oils in suspension, are allowed to settle, and again the aqueous portion, after separation from the oils, is used to dilute the crude acetone.

The oils are divided into two groups, namely: (1) *white acetone oil*, which is obtained by dilution of the last runnings, as described above; most of this product boils between 70° and 130° C.: (2) *yellow acetone oil*, which boils between 130° and 250° C. and is obtained directly from the still at the end of the operation, or from the oils which separate on diluting the crude acetone.

The *white oils*, separated from the last runnings, are accumulated to form one charge and are then rectified in a column still. The first fraction consists of the acetone present in the oils; this is followed, with moderately sharp demarcation, by *methyl ethyl ketone*; and it is easily possible with a steam pressure of about 7 atm. to drive over fractions which are completely free from water, and the boiling-point of which approaches 140° C. Direct steam is then passed into the residue, and the

distillate—yellow acetone oil—is separated mechanically from the water in a Florentine receiver.

The acetone oils which separate out on dilution of the crude acetone are similarly collected to form one charge, and the low-boiling components (acetone and methyl ethyl ketone) are distilled off by indirect steam. These fractions are added to the aqueous solution of crude acetone after it has been separated from the oils. When the low-boiling components have been removed, direct steam is passed in and the *yellow acetone oil* is distilled over; this product is then mixed with similar products obtained as last runnings from the various processes of rectification.

The water which condenses with the yellow acetone oil during distillation in steam is separated from the oil and used for the dilution of crude acetone.

In order to be in a position to carry out the various operations described above, several column stills of suitable capacity must be provided. It is advisable to use separate stills for the first distillation, the rectification of the middle runnings and the treatment of the oils; in this way, the same products always undergo rectification in the same apparatus, and the troublesome task of cleaning the latter after every operation is avoided.

In starting up the process it is usual to collect the products in carboys or barrels. After a certain degree of equilibrium has been established, and the operators have acquired the necessary experience, the products are run into tanks directly from the condensers, each tank being capable of holding sufficient liquor to form a charge for the still.

The flow-sheet on page 342 illustrates the usual method of conducting the process and the manner in which the distillate is divided up into various fractions.

The *white acetone oils* (B.P. 70–130° C.) find a ready market in the celluloid industry and in other industries where gelatinising agents are required. In certain countries, for example, France and Austria, the white oils are added to denaturing wood-spirit.

The *yellow acetone oils* are also used for denaturing purposes, and as solvents, for example, in the purification of crude anthracene.

For a description of the commercial tests which are usually applied to acetone oils see under "Acetone" in the Analytical Section (p. 396).

The above process of separating acetone from the crude product is similar in principle to the separation of pure methyl alcohol from crude wood-naphtha.

We have seen already that in the latter case it is possible to carry out the process continuously. It is equally feasible to employ a continuous process for the recovery of pure acetone from crude acetone, after separating the bulk of the oils by dilution with water.

The continuous stills employed for the purpose are similar to those used for the wood-naphtha process. Most of the intermediate fractions mentioned above no longer appear ; consequently the whole process is rendered more simple and less costly. Moreover, the initial cost of one continuous still is considerably less than that of several intermittent stills.

CHAPTER XVII

TREATMENT OF CRUDE WOOD-TAR AND TAR-OILS

THE origin of the various kinds of wood-tar has already been discussed on page 66. The following main varieties were distinguished :—

1. *Settled hardwood-tar*, heavier than pyroligneous acid and separated from the latter by settling the mixture. This product possesses the following average composition :—

	Per cent.
Acetic acid (100 per cent)	2·00
Wood-spirit „ „	0·65
Water	17·75
Light oils	5·00
Heavy oils	10·00
Soft pitch (including loss as gas)	64·60

2. *Dissolved hardwood- and softwood-tar*, which remains dissolved in pyroligneous acid after separation of the settled tar and is obtained as the residue after distillation of the acid. Approximate composition :—

	Per cent.
Acetic acid	8
Water	32
Hard pitch (including loss as gas)	60

3. *Settled softwood-tar* (“Swedish” or “Stockholm tar”), which is obtained by settling softwood pyroligneous acid; this product is mostly lighter than the acid and possesses the following approximate composition. (Average of the fractions mentioned on page 72) :—

	Per cent.
Pyroligneous acid	12
Terpenes, hydrocarbons	30
Softwood-tar	58

1. Treatment of Settled Hardwood-Tar.—Formerly, this product was always submitted to distillation by direct fire,

in order to recover hydrocarbons for illuminating and lubricating purposes, and also phenols and pitch. Nowadays, however, it is unusual to carry the distillation beyond the point at which water, acetic acid, wood-naphtha and light oils are eliminated from the tar.

This operation is performed most conveniently in a copper still (similar to that shown in Fig. 40) fitted with a copper steam-coil and connected with a copper condenser which delivers into a Florentine receiver. The tar is heated to 140–150° C. by indirect steam, and the main bulk of the water, acetic acid, wood-naphtha and light oils is distilled over. The Florentine receiver separates the aqueous portion of the distillate from the supernatant light oils. The aqueous solution is returned to the pyroligneous acid produced in the wood-distillation process. The oils are either burnt directly or used for the generation of power. Up to the present, no other application has been found for these products, mainly on account of their unpleasant odour which is difficult to remove.

Indirect heating alone does not free the crude tar completely from the above-mentioned components; it is therefore the general practice to assist the distillation by introducing direct steam, until the amount of acetic acid present in the distillate is no longer worth recovering. The residue then consists of dehydrated and de-acidified tar which still contains the heavy oils. This distillation can be carried out, of course, in direct-fired stills, but the tar then shows a great tendency to froth over, especially in the initial stages of the process. For this reason it is customary to use steam as the heating agent, as long as the sole object of the process is to dehydrate the tar.

If, in addition to the recovery of acetic acid, naphtha, etc., it is desired to produce heavy oils and pitch, and eventually to prepare creosote oil and possibly creosote from the heavy oils, the distillation of tar must be carried out by direct fire. The boiling-points of the last fractions are so high that it is no longer possible to drive over these fractions by means of high-pressure steam or even by reducing the pressure in the still and heating with superheated steam.

The tar stills used for this purpose (see Fig. 46) are similar to those employed for the distillation of coal-tar. In view of the amount of acid present in the wood-tar, however, the stills in this case are not constructed of steel; instead, cast-iron is used for the lower portion and copper for the upper

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portion. Owing to the use of cast-iron the size of the still must necessarily be limited; as a rule the capacity rarely exceeds 3000-5000 litres.

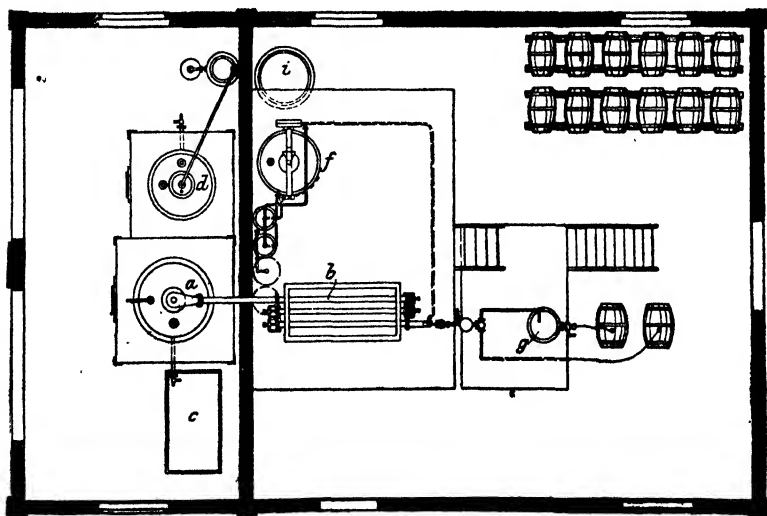
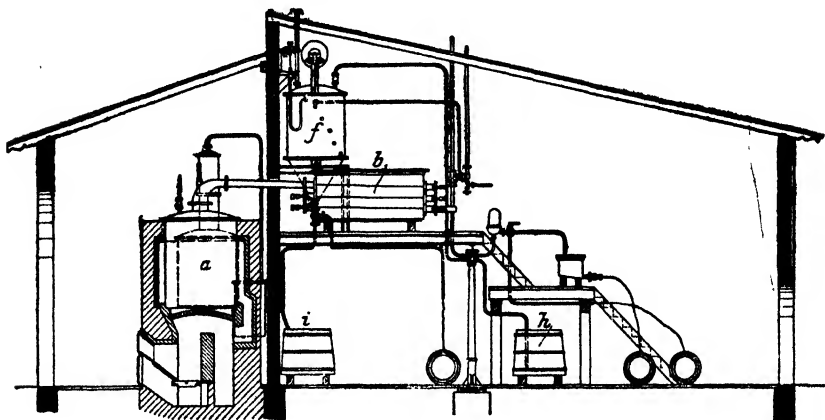


FIG. 46.—PLANT FOR THE DISTILLATION OF HARDWOOD-TAR AND CONVERSION OF THE CRUDE DISTILLATES INTO FINISHED PRODUCTS.

a, tar still ; *b*, condenser ; *c*, pitch cooler ; *d*, oils still ; *f*, creosote oil extractor and washer ; *g*, Florentine receiver ; *h*, collecting vat for creosote oil ; *i*, collecting vat for creosote.

The still consists of a cast-iron cylinder, usually with a concave bottom. Just above the lower edge of this cylinder is the pitch outlet-pipe, which must be protected against the action of fire and must be wide enough to allow the pitch to run out freely without risk of obstruction. The cover is generally made of copper: it is connected by means of a copper head-piece with the condenser, which is usually of the type shown in Fig. 18, this being the most suitable form for the purpose, as the tubes are wide and therefore can easily be cleaned.

The head-piece is fitted with a thermometer, the bulb of which is kept above the surface of the tar. The still is often provided with a safety valve, which, if the still happens to boil over, must also serve as a channel of escape for the frothing tar without giving rise to the danger of fire. An inlet pipe, fitted with a cock for charging the still, completes the equipment. The delivery pipe and the condenser-tubes must be wide enough to prevent choking by any solid matter which may separate out during the distillation.

The condenser delivers into an observation chamber which allows the flow of the distillate to be observed. A siphon pipe connects the condenser with the observation chamber, and acts as a liquor trap serving to separate the non-condensable gases from the liquid products; the gases escape through a vertical pipe which is fitted behind the siphon pipe (see Fig. 46).

The still is usually charged by means of a pump, the suction pipe of which extends to the bottom of the tar-pit or vat.

The tar-pit, or vat, contains a copper coil through which waste steam can be passed for the purpose of warming up the tar and rendering it less viscous and easier to pump. While the pump is in operation, a measuring stick is dipped into the pit from time to time, in order to ascertain when a sufficient quantity of tar to form a charge has been delivered to the still.

After the still is charged, firing is begun, and if the brickwork is cold, as is usually the case, the heating is conducted vigorously until the cover of the still just begins to grow warm. The stoker must then moderate the heating and wait until the distillate appears at the outflow of the condenser. Firing must now be carried on with extreme caution, since the tar at this stage shows a great tendency to boil over. The first components to vaporise are the pyroligneous acid and the

wood-naphtha, which appear at the outlet of the condenser as a yellowish aqueous distillate with light oils floating on the surface.

The distillate flows from the observation chamber into a copper Florentine receiver, which separates the pyro-ligneous acid from the light tar-oils and returns it to the tar-free acid derived from the wood-distillation process. The light tar-oils pass into a separate vessel. When the thermometer indicates a temperature of about 110°C. , the rate of distillation usually diminishes, since the main bulk of the water has been driven over, and only a small amount remains in the residue. During the earlier stages of the process, the water lowers the boiling-point of the mixture very considerably; as soon as it is removed, the boiling-point rises rather suddenly. The strictly controlled rate of heating which has been maintained during the first period is now insufficient to keep the contents of the still in a state of ebullition; consequently, distillation practically ceases and only sets in again when the necessary amount of heat has been supplied to the still. The temperature then rises rather rapidly, and from this point onwards any risk of the tar boiling over is practically absent. Firing may therefore be carried on vigorously and the distillation accelerated.

Provided that the plant has been properly designed in the first place, no serious danger is likely to arise in the event of the tar boiling over. Care should be taken to place the condenser outlet at an adequate distance from the furnace; further, it is always advisable to erect a wall between the tar still and the condenser.

The greatest danger may arise from the action, in certain circumstances, of the ordinary safety valve which is fitted to the cover of the still. If the tar starts to froth or boil over, the valve will open owing to the increase in pressure, with the result that the tar will flow out on to the cover, trickle down the convex surface of the latter, and run down the brickwork to the ground. When this happens, it is practically certain that the liquid, while running down the brickwork, will become ignited, hence the safety valve may be of more harm than use. On the other hand, if the delivery pipe and condenser-tubes are sufficiently wide, and especially if the condenser and still are separated by a fireproof wall, the only serious trouble which can arise is pollution of the condenser tubes. In these

conditions any real danger is absent, and loss of tar can be entirely avoided by fitting to the condenser outlet-pipe a return pipe which delivers into the tar-pit and, normally, is kept closed by means of a cock. If boiling-over occurs, it is only necessary for the operator to turn the cock, in order to divert the overflowing tar to the tar-pit. There is no objection to the use of safety valves, etc., on the still, but special measures must be adopted to prevent the tar from flowing on to the cover and thence possibly into the furnace. The best plan is to arrange that all safety appliances which will afford a channel of escape for the tar, if it boils over, shall open into pipes which will convey the tar away from the still. If proper care is exercised and the operator has had sufficient experience in running the plant, boiling-over very seldom occurs. The expedients which are often adopted to prevent boiling-over, such as drawing the fire, opening the fire-door and flue-dampers, spraying the cover of the still with water, etc., generally prove useless, since it is rarely possible to counteract the effect of the heat radiated from the brickwork setting. A very sound practice is to fit an open steam pipe into the head-piece, so that, in case of overflow, the delivery pipe and condenser-tubes can be cleaned rapidly and easily.

After the main bulk of the pyroligneous acid and light oils has been driven off—the thermometer then indicating about 110°C .—the higher-boiling oils begin to come over. These oils contain only a small amount of pyroligneous acid and continue to flow until a temperature of about $250\text{--}260^{\circ}\text{C}$. is reached. These temperatures vary, of course, in every tar still, according to the position of the thermometer.

The oils which come over after the pyroligneous acid period are collected in two separate fractions, namely: (1) oils lighter than water, (2) oils heavier than water. These products are not yet marketable since they contain considerable amounts of dissolved tar, which has been carried over by the oily vapours. As soon as the temperature—measured within the vapour zone of the still—reaches 260°C . the process is usually complete, the residual pitch being by that time sufficiently free from oils and possessing the proper consistency. Towards the end of the operation, samples of pitch are withdrawn from time to time, in order that the operator may have some indication as to the right point at which to stop the distillation. It should be noted that, after the heating has ceased and the

fire has been drawn, distillation still goes on, owing to radiation of heat from the incandescent brickwork. Firing must therefore be stopped some time before the pitch has reached the desired consistency. If this precaution is omitted, the contents of the still may easily become coked or the pitch may boil over, with very unpleasant consequences.

The pitch should not be run off immediately after completion of the process, since the product, while still very hot, shows a tendency to take fire on coming into contact with the air. This danger can be prevented by allowing a few hours to elapse between the end of the distillation and the discharge of the pitch, the fire-door and flue-damper being left open during this period.

Usually, the pitch outlet becomes stopped up with particles of dirt or tar-coke, but if the cock is so designed that an iron rod can be thrust right through it from the front, without the necessity of removing the plug, it is usually an easy matter to clear away any obstruction. The pitch then flows out rapidly into the pitch-pit, or better into an iron pitch-cooler, situated at the foot of the tar still. In this vessel the pitch forms a smooth shallow layer which cools rapidly; when cold, it can be easily broken up and removed, after which it is packed into suitable containers and is then ready for shipment.

In most of the wood-distillation factories which undertake the distillation of wood-tar, the process is restricted to the above-mentioned operations, the manufacturers endeavouring to dispose of the light and heavy oils and also the pitch to the best possible advantage. At present, the pitch finds the readiest sale.

Formerly, the light oils, after undergoing the necessary purification, were used for illuminating purposes; but as a result of the development of the petroleum industry, and the distillation of coal tar and lignite on an enormous scale, vast quantities of illuminating and lubricating agents have been placed on the market, and the wood-tar oils are no longer able to compete with these products.

Usually, it is possible to dispose of the heavy oils from beech-wood tar, since these products serve as the raw material for the manufacture of creosote, which for many years has been utilised in medicine as a remedy for tuberculosis, etc. In wood-distillation factories the treatment of heavy oils for this purpose is rarely carried beyond the production of fractions rich in

creosote; these are sold to factories specially engaged in the manufacture of the latter product.

During the distillation of tar by direct fire, three different kinds of oil are obtained:—

1. Oils, lighter than water, which come over with the pyroligneous acid in the early stages of the distillation and float on the surface of the acid.

2. Oils, lighter than water, which come over after the pyroligneous acid period.

3. Oils, heavier than water, which come over subsequently.

Each of these fractions contains acetic acid. In addition, wood-naphtha comes over with fraction (1), and fractions (2) and (3) carry over a certain amount of tar. None of these products is ready for sale, since the consumer usually demands an article which is free from acetic acid and tarry matter.

The method of working-up these fractions is indicated in the flow-sheet on page 352. The tar is removed from fractions (2) and (3) by distilling these products in plant similar to that employed for the distillation of crude tar. The tarry components constitute the residue at the end of the process, and a portion of the pyroligneous acid together with a certain amount of oil appears as “first runnings,” which are usually very highly concentrated. The acid is separated from the oils in a Florentine receiver.

All intermediate portions of the distillate which are heavier than water are combined, and the mixture is subsequently freed from acid by washing with water or sodium carbonate solution.

Washing is best carried out in a vertical copper agitator—similar to the lead-lined agitator used in refining petroleum, washing crude benzine, etc.—as shown in Fig. 46, *f*.

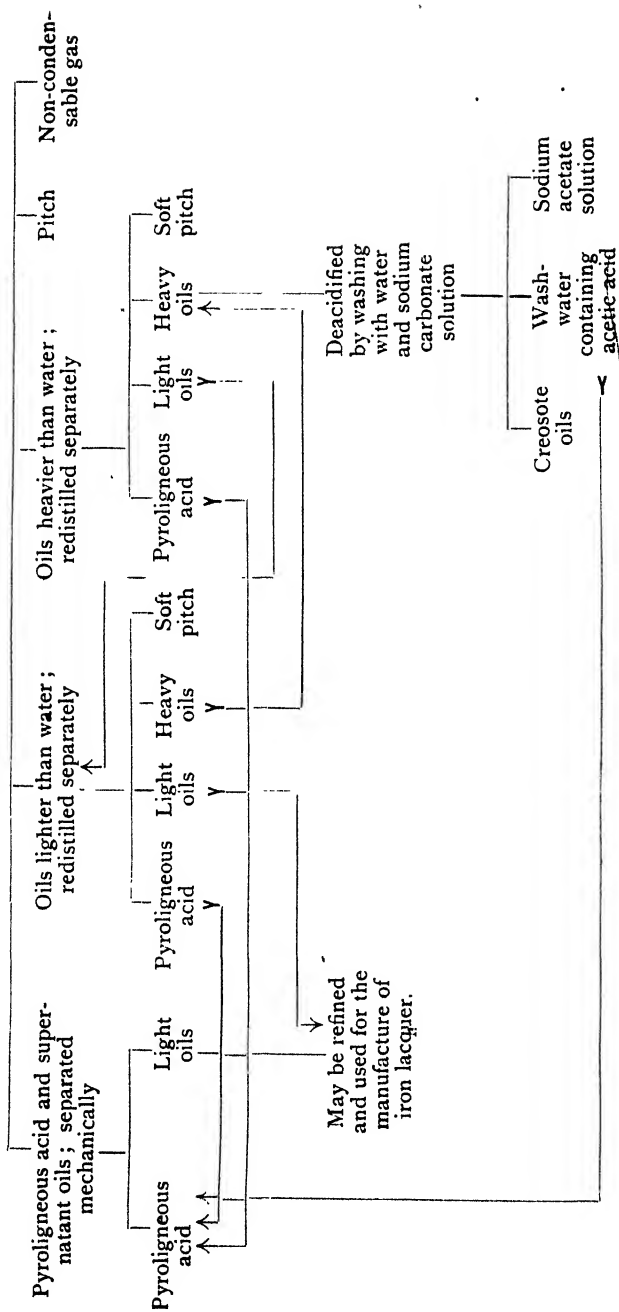
On allowing the mixture to settle, the washed oils collect in a layer below the washing agent and are run off separately.

The wash-water, which contains free acetic acid, is mixed with the pyroligneous acid, and the solution of sodium acetate which results after washing with sodium carbonate is evaporated.

The washed oils contain about 50 per cent of phenols and serve as raw material for the manufacture of pure creosote.

Manufacture of Crude Creosote.—The treatment of the

SETTLED HARDWOOD TAR, DISTILLED BY DIRECT FIRE



washed oils for crude creosote is a comparatively simple process. The plant required for the purpose is shown in Fig. 46 as forming part of a complete installation for the treatment of tar and tar-oils. The washed oil is run into a special tank from which it is pumped or injected into a mechanical mixer or agitator. The upper portion of this vessel is cylindrical and the lower portion funnel-shaped (Fig. 46, *f*). The vessel is provided with a cover and is fitted with stirring apparatus which acts like a ship's screw and is capable of converting two non-miscible liquids into an emulsion. In this agitator the creosote oil is extracted systematically with weak caustic soda solution, which dissolves all the phenols present; the hydrocarbons remain undissolved and may be run off separately.

The alkaline solution of creosote obtained in this way contains a certain quantity of suspended matter, chiefly hydrocarbons; these are removed by blowing in a current of steam until a sample of the condensed vapour appears practically free from oil.

The crude creosote is then fractionally precipitated from the alkaline solution by treating the latter with dilute mineral acid. For this purpose it is usual to employ either hydrochloric or sulphuric acid, but it is also possible to decompose the alkaline creosote solution by means of carbon dioxide (flue gases).

The solution is stirred during the addition of the acid and is then allowed to settle. The crude creosote separates out on the surface; the salt solution, after it has clarified, is run off by means of suitable arrangements on the apparatus.

Manufacture of Pure Creosote.—The creosote fractions obtained by the above process represent only a crude product which, in the first place, must be redistilled for the purpose of eliminating all non-volatile components such as tar.

The process of isolating pure creosote or pure guaiacol from the redistilled crude product is rather lengthy. It consists in redissolving the product in caustic soda, blowing steam through the solution, fractionally decomposing this solution by the addition of mineral acid, treatment of the creosote with oxidising agents and finally fractional distillation.

The plant required for these operations is similar to that described above for the manufacture of crude creosote.

The fractional distillation is usually carried out in stoutly constructed copper stills fitted with copper columns. Copper

condensers are used during the earlier part of the distillation, and silver condensers in the later stages.

No particular difficulties are experienced in manufacturing creosote from creosote oil, provided that the specific gravity of the product is not required to exceed 1.070.

It is much more difficult, however, to obtain a reasonable quantity of creosote of such high grade that, on treatment with alcoholic potash, it rapidly becomes solid owing to the formation of potassium guaiacol, it dissolves in caustic soda to form a clear colourless solution, and it possesses a specific gravity exceeding 1.08 at 15° C.

Only a very small number of wood-distillation factories undertake the manufacture of creosote. The main bulk of the output is produced in chemical factories, partly from creosote oil and partly by synthetic processes.

2. Treatment of Dissolved Tar.—The essential differences between settled tar and dissolved tar, and the probable origin of the latter, have already been discussed on pages 66–72.

On distillation, soluble tar gives only two products, namely:—

1. Pyroligneous acid, containing a relatively large proportion of acetic acid.

2. Very brittle pitch.

In this case the oily fractions which characterise settled tar are completely absent.

Dissolved tar always tends to retain a very considerable quantity of acetic acid, as indicated by the composition given on page 344.

The tar itself is a practically worthless product of wood-distillation, and the only object in treating it further is to recover the acetic acid which can no longer be removed by heating the tar with indirect steam at 6–8 atm. pressure.

Recovery of acetic acid may be effected by distilling the tar in a fire-heated still. This process, however, is not altogether simple, since the tar, when heated to a moderately high temperature, shows a great tendency to froth over and become coked, thus giving rise to all manner of inconvenience.

A much more satisfactory method is to heat the tar with indirect steam and at the same time to introduce direct steam, exactly as described above for the dehydration of settled tar.

This operation is carried out in a copper still (similar to that

shown in Fig. 40) fitted with open and closed steam-coils. The tar is heated first of all by means of the closed coil alone, until it has acquired the temperature of the steam

Direct steam is then introduced cautiously, the temperature being kept constant by means of the closed coil, and the operation is allowed to proceed in this manner until the amount of acetic acid present in the distillate is so small that it is no longer worth recovering.

As a rule it may be reckoned that the volume of the distillate obtained in this way will be equal to the original volume of tar ; it will contain, of course, nearly the same amount of acetic acid as was present in the tar.

As soon as the operation is complete, the residual pitch is run out of the still. On cooling, this product sets to a brittle mass which possesses no valuable properties and in most cases can only be utilised as fuel.

The tarry product which is obtained from the Meyer tar-separator may be regarded as a mixture of settled tar and dissolved tar. It undergoes exactly the same treatment as described for hardwood-tar, that is, distillation in a direct-fired still if the object is to isolate the tar-oils, or simple heating with direct and indirect steam simultaneously if the object is merely to recover the acetic acid and the small quantities of wood-naphtha still present in the tar.

The pitch which this kind of tar furnishes is intermediate in properties between the soft-pitch from the settled tar and the brittle hard-pitch from the dissolved tar. Its quality, however, is sufficiently satisfactory to render it just as marketable as the former.

3. Treatment of Softwood-Tar¹ and Tar-oils.—Softwood-tar differs in many important respects from the tar derived from non-resinous hardwood.

In commercial value these two varieties of tar exhibit a striking difference. Hardwood-tar is always difficult to sell in large quantities, and fetches only a comparatively low price—seldom more than 3s.-4s. per 100 kilos.

Softwood-tar, which is known variously as "Stockholm tar," "Swedish tar," "Finland tar" and "Russian tar," and

¹ The manufacture of oil of turpentine by distilling softwood in a current of steam or by extraction processes does not fall within the scope of this book, which is only intended to deal with the methods, objects and products of the destructive distillation of wood.

is exported from those countries in considerable quantities, can easily be sold in any quantity, and at a much better price than that obtainable for hardwood-tar.

Softwood-tar always contains products of the destructive distillation of rosin, but these products are absent from hardwood-tar.

Softwood, like hardwood, is composed chiefly of cellulose, lignin and water. On destructive distillation, therefore, it produces acetic acid and wood-naphtha, though in relatively smaller quantities than hardwood, together with the various decomposition products which constitute the mixture known as "tar."

It is obvious, therefore, that softwood-tar must contain all the components which are present in hardwood-tar.

In addition, however, softwood contains a mixture of *oil of turpentine* and *rosin*, and this may constitute as much as 20 per cent by weight of the wood, as the author found on examining certain species of pine in the southern states of America.

The root-stumps of European conifers, when deprived of the sapwood, often contain 15-20 per cent of oil of turpentine and rosin.

This mixture is known as "crude turpentine." It is the substance which flows spontaneously from wounds made in the trunks of conifers, and is obtained in large quantities in America, France and other countries by "tapping" the trees.

Rosin is the anhydride of abiëtic acid, and is known commercially as "colophony."

Oil of turpentine boils at 160-170° C., but is readily volatile in water vapour, even below 100° C. Hence, when air-dry softwood is carbonised, the oil of turpentine comes over with the water which is expelled from the wood in the early stages of the process.

As the internal temperature of the carbonising apparatus increases, the rosin melts and flows out on to the surface of the wood. Since the internal temperature soon reaches 180° C., it follows that the thin layers of rosin on the individual pieces of wood must also undergo destructive distillation, with the formation of the same decomposition products as are obtained when rosin is distilled alone, namely, (1) light oils, known as "*rosin-spirit*" or "*pinoline*," (2) heavy oils, known as "*rosin-oils*," and (3) a residue of so-called "*rosin-coke*."

As mentioned previously, it is almost impossible to maintain a uniform temperature throughout a charge of wood undergoing distillation in a large carbonising apparatus. Consequently, a certain amount of rosin is decomposed during the earliest stages of the carbonisation of softwood, that is, while oil of turpentine is still coming over with the water expelled from the wood. As a result, the actual oil of turpentine becomes mixed with rosin-spirit.

If the carbonising apparatus is sufficiently large, the process resolves itself into more or less definite stages. At first, the oily portion of the distillate consists of oil of turpentine alone, later, of a mixture of oil of turpentine and pinoline, and eventually, of these two products mixed with rosin-oils.

At this stage, the internal temperature of the carbonising apparatus has reached the point at which cellulose and lignin also begin to decompose with the formation of the normal components of wood-tar, and these pass into the distillate.

Consequently, the oily product obtained by carbonising softwood is never pure oil of turpentine, but a mixture of the latter with varying amounts of pinoline, rosin-oils and the usual components of wood-tar.

This mixture is known as "crude pine-oil," also as "German" or "Russian oil of turpentine."

Reference to the tables given on page 72 will show that the early fractions of the distillate which is produced on carbonising softwood contain only small quantities of tar, rosin-oils and pinoline and a relatively large proportion of terpenes, whereas the last fractions consist mainly of tar and rosin-oils and contain little pinoline and an even smaller proportion of terpenes.

Owing to the presence of terpenes these fractions are mostly lighter than pyroligneous acid; they generally float on the surface of the acid, especially if the latter is not cooled down too far.

In order to separate the oil of turpentine as completely as possible from the remaining decomposition products of wood and rosin, it is usual, as indicated above, to collect the distillate in fractions, each of which corresponds to a certain range of specific gravity (see p. 72).

These fractions may be described as "crude pine-oil" or "crude tar," according to their composition.

The smaller the carbonising apparatus—and therefore the

smaller the charge of wood undergoing carbonisation—the more closely does the composition of the earlier fractions approach that of the later fractions. The larger the carbonising apparatus, the easier it is to obtain the oil of turpentine, originally present in the wood, as a separate product, particularly if a special tar-separator is interposed between the carbonising apparatus and the condenser, or if the wood is carbonised in ovens fitted with bottom outlets. In this connection, reference may be made to the various types of Swedish oven described in Chapter XI, and it should also be noted that a large proportion of the softwood-tar manufactured in Finland and Russia is produced in kiln-like structures provided with bottom outlets.

In every carbonising apparatus of this type, the hot gases and vapours are forced to pass downwards through layers of wood which show a gradual decrease in temperature and from which moisture is still being driven off; consequently, by the time the gases and vapours have reached the outlet, they have become cooled to such an extent that tarry matter condenses out.

A siphon situated at the bottom of the oven separates the *condensed tar*, with the result that the products passing into the condenser are relatively free from tar but contain a considerable proportion of terpenes.

The *condensed liquor* is passed through a Florentine receiver, which separates the mixture of oils from the pyroligneous acid. Only very exceptionally can this mixture be sold as a finished product; as a general rule it must be refined beforehand, for the purpose of isolating pine-oil which at least is free from tar, and tar which contains relatively little pine-oil.

The first operation in the refining process is nearly always carried out in the wood-distillation factory, and consists in distilling the crude fractions in a copper still fitted with copper steam-coils and connected with a copper condenser (see Fig. 47). The charge is heated by indirect steam, and direct steam is then introduced, exactly as described for the dehydration of settled tar and the de-acidification of soluble tar (p. 345).

The distillate, which may be collected in fractions if desired, constitutes the *pine-oil* of commerce; the residue consists of tar, free from water and pyroligneous acid, which, after having cooled sufficiently, may be run directly into containers for export.

The value of this tar varies according to the particular fraction from which it has been derived (see table, p. 72). The more valuable tar is obtained from the earlier fractions, the less valuable from the later fractions.

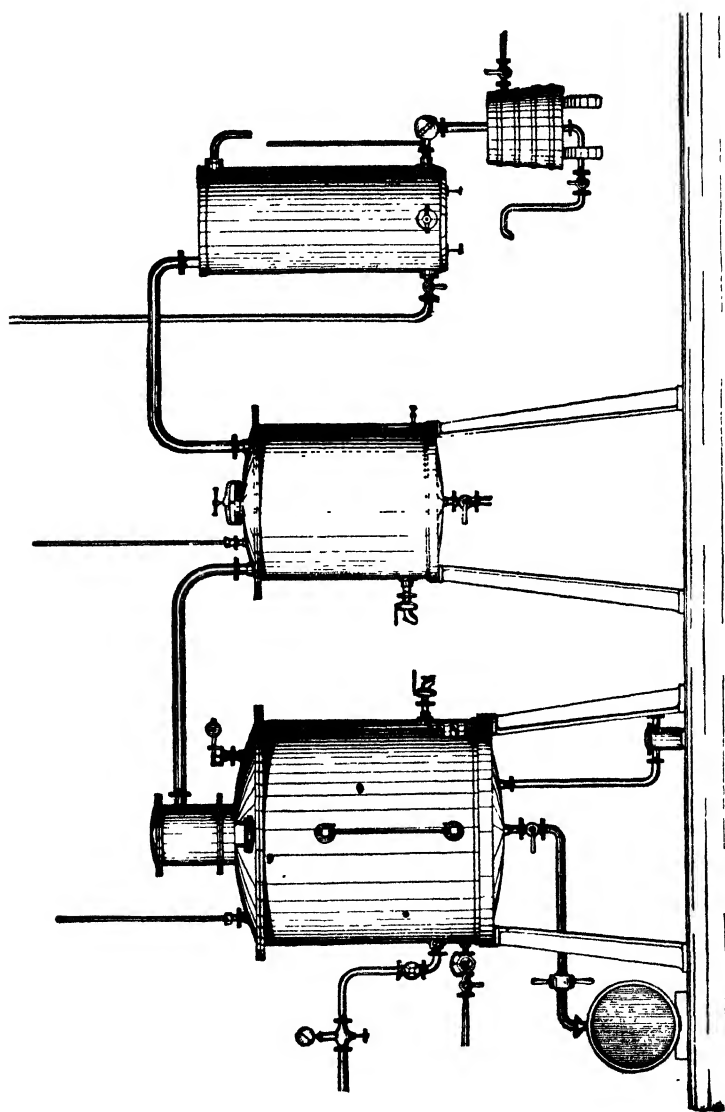


FIG. 47.—PLANT FOR ELIMINATING TAR FROM CRUDE PINE-OIL AND CONCENTRATING CRUDE SOFTWOOD-TAR.

The relative value of the tar is judged chiefly by its colour when spread out in a thin coat on light-coloured wood. The lighter its colour, the more rapidly it dries, the more sticky its nature and the more resistant it is to the action of water, the better is its quality.

The degree of purity of commercial pine-oil depends of course on the particular process by which it has been manufactured. As mentioned above, pine-oil is chiefly produced in a more or less primitive fashion from brickwork carbonising apparatus in Russia and Finland. In this case there is no question of dehydrating the tar or of eliminating tar from the pine-oil, the product being sold simply in the form in which it is obtained from the carbonising apparatus. This product is a brownish-black liquid with a strongly empyreumatic and penetrating odour; it contains about 10 per cent of tar, consequently its specific gravity is relatively high, namely, 0.870–0.890.

The composition of this product is extremely complex, and has not been fully elucidated as yet, in spite of investigation by various workers.¹

As stated above, the fundamental components of crude pine-oil are (1) *terpenes*, partly representing original components of the wood, and partly derived from the destructive distillation of rosin; (2) *hydrocarbons*, which have been formed as a result of the destructive distillation of cellulose, lignin and rosin.

In addition, crude pine-oil contains free fatty acids of the formic acid series, especially acetic acid; all the components of wood-naphtha, including acetone, methyl alcohol, allyl alcohol, etc.; aldehydes and a considerable quantity of phenols.

Aschan has also detected the presence, in varying proportions, of the following:—

Furanes (furane, silvane, dimethylfuran).

Hydrocarbons of the benzene series (benzene, toluene, xylene).

Diketones of the aliphatic series (diacetyl, acetyl propionyl).
Furfural.

- Unsaturated hydrocarbons.
- Alkyl quinones.

¹ Atterberg, Ber. 1880, **13**, 879. Harries, Ber. 1904, **31**, 37. Aschan, Zeit. angew. Chem. 1907, **42**, 1811.

In addition to these substances, the crude pine-oil always contains a certain amount of tar.

In refining pine-oil, the chief task is to isolate the terpenes, as far as possible, from a mixture composed of substances varying widely in chemical properties, and to obtain a product which shall closely resemble American oil of turpentine in its physical constants, external appearance and odour.

Owing to the rapacious manner in which the stocks of conifers in the southern American states (Georgia, Virginia and Mississippi) are being tapped for turpentine, it is probable that at a not very remote period the output of American oil of turpentine will diminish very considerably. In this case it will be necessary to consider the possibilities of manufacturing a substitute for oil of turpentine by the destructive distillation, on a more extensive scale, of the richly resinous roots of conifers which are available in Russia, Finland, Sweden and many other countries.

Already this industry is quite remunerative, especially when, as is frequently the case, the price of oil of turpentine happens to be so high that it almost prohibits the use of that article for outside paint-work, etc. In this connection a wide market is open for refined pine-oil, but only if the characteristic odour, which is very disagreeable and causes headache, has been absolutely eliminated.

According to Aschan, the pungent odour of pine-oil is due chiefly to the presence of diketones; certain other components are responsible to some extent, for example allyl alcohol and also sulphur compounds, as the above author has demonstrated.

The process of refining pine-oil and removing all impurities which are likely to interfere with the quality of the finished product comprises not only careful fractional distillation but also suitable chemical treatment.

Obviously, there can be no hope of manufacturing a product which is identical in all its properties with American oil of turpentine—an article composed entirely of terpenes. The most that can be obtained by the refining process is a finished product which *resembles* American oil of turpentine.

On considering the above-mentioned components of crude pine-oil, it will be quite clear that the removal of the volatile fatty acids, phenols and tar should offer no difficulty.

In the first place, the crude pine-oil is heated to 130–150° C.

by means of indirect steam, and direct steam is then introduced (see Fig. 47); in this way all volatile products, even those with boiling-points exceeding 200°C ., are separated from the tar, which remains behind in the still. The distillate is collected in fractions, and the components which come over below 150° —that is, before direct steam is introduced—constitute the first fraction.

The relative amounts of these components vary widely, and depend on the manner in which the crude pine-oil has been manufactured.

This fraction contains the substances which are most largely responsible for the unpleasant odour of crude pine-oil, namely, sulphur compounds, diketones, and the components of wood-naphtha, especially allyl alcohol.

The separation of the low-boiling components during the first operation is already a most important step in the process of purification, and distinctly improves the odour of the pine-oil. It is obvious that a certain proportion of the terpenes will also come over with the first fraction, but this sacrifice must be made in order to obtain the main bulk in a higher state of purity (cf. manufacture of pure methyl alcohol, p. 254).

The first fraction also contains the greater proportion of the volatile acids present originally in the crude pine-oil.

The main bulk of the distillate from the first operation already possesses a comparatively pure odour; it still contains phenols, aldehydes, ketones and hydrocarbons, but only a small amount of volatile acids.

The next operation consists in washing the product with caustic soda solution of definite concentration (the correct proportions must be ascertained by experiment) in vertical agitators similar to those already described for the treatment of heavy wood-tar oils (see Fig. 48).

By this means, the volatile fatty acids and phenols are neutralised, the aldehydes resinified, and the ketones converted into high-boiling condensation products which can be eliminated during the subsequent process of rectification.

After treatment with caustic soda it is usual to wash the product in the same apparatus with moderately concentrated sulphuric acid, which removes the bulk of the furanes and the unsaturated compounds.

The sulphuric acid must not be too concentrated, otherwise it will act on the terpenes and convert them into high-boiling

condensation products. During this treatment the acid becomes dark-coloured owing to its action on the impurities present in the pine-oil.

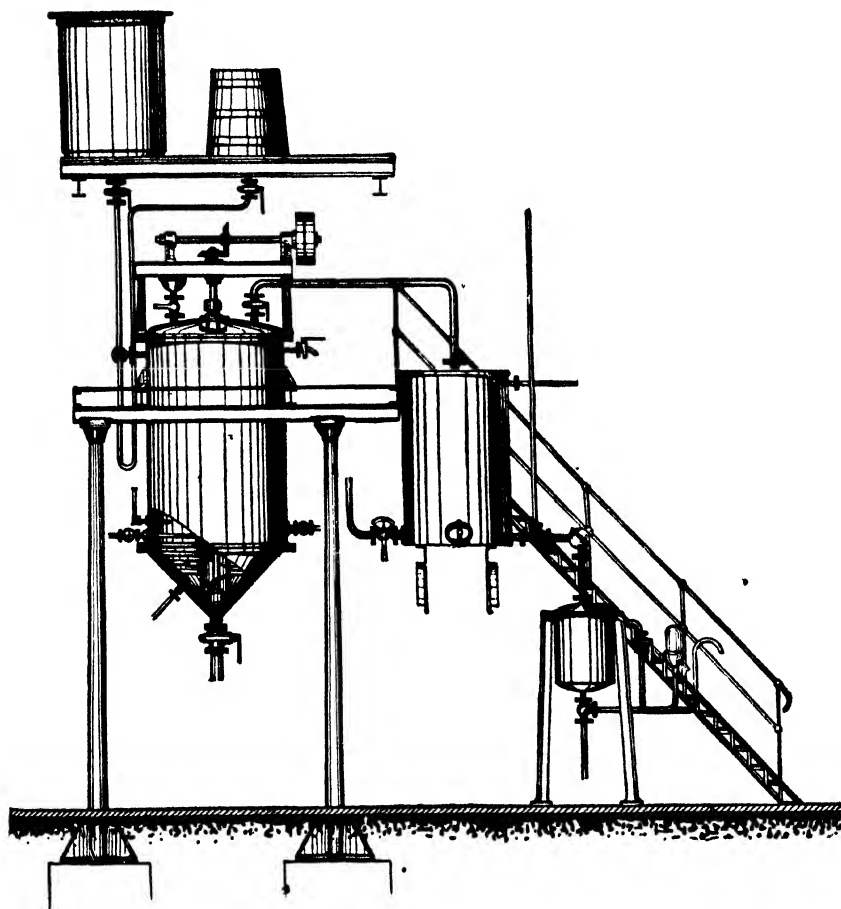


FIG. 48.-VERTICAL MIXING AND DISTILLATION APPARATUS FOR THE TREATMENT OF PINE-OIL WITH ALKALI AND ACID.

After allowing the mixture to settle, the acid layer is run off and the residual pine-oil is washed several times with water and finally with dilute caustic soda.

The product remaining in the washing apparatus possesses an orange colour and is practically free from all the original

impurities with the exception of the hydrocarbons; the latter cannot be removed by any of the above-mentioned processes of purification.

It still contains a portion of the conversion products resulting from the treatment with caustic soda and sulphuric acid, but these substances possess very high boiling-points and can therefore be separated from the mixture of terpenes and hydrocarbons during the subsequent process of rectification.

The final operation consists in eliminating the hydrocarbons to such an extent that the resultant product boils at approximately the same temperature as American oil of turpentine. The only method by which this separation can be effected is fractional distillation.

The distillation is carried out in column stills, which operate on exactly the same principle as the stills already described for the *intermittent* distillation of wood-naphtha, acetic acid and acetone. Heating may be carried out by direct fire, or by passing a current of steam through the charge; the most efficient process, however, consists in distilling the product under reduced pressure in an apparatus similar to that shown in Fig. 49—using high-pressure steam as the heating agent.

High-pressure steam cannot be employed when the distillation is carried out under normal pressure, since the mixture of terpenes and hydrocarbons boils above 160°C . By reducing the pressure, it is easily possible to lower the boiling-point to $110\text{--}120^{\circ}\text{C}$. and therefore to fractionate pine-oil in a column still just as efficiently as any other mixture which produces fractions boiling up to 120°C .

In the vacuum apparatus, the condenser delivers into one of two vacuum receivers, which are connected with an air-pump and are used alternately. As soon as one receiver is full, the other is brought into circuit by means of a by-pass connection; the first one is emptied, and after being evacuated is again ready to receive the distillate.

By fractional distillation in an apparatus of this type, it is easily possible to obtain a water-white product which is free from non-volatile residue and boils within the limits specified for genuine oil of turpentine.

Although it is impossible to produce a *refined pine-oil* which possesses exactly the same odour as American oil of turpentine, it is undoubtedly possible, as a result of the processes described above, to obtain a product which has lost every trace of

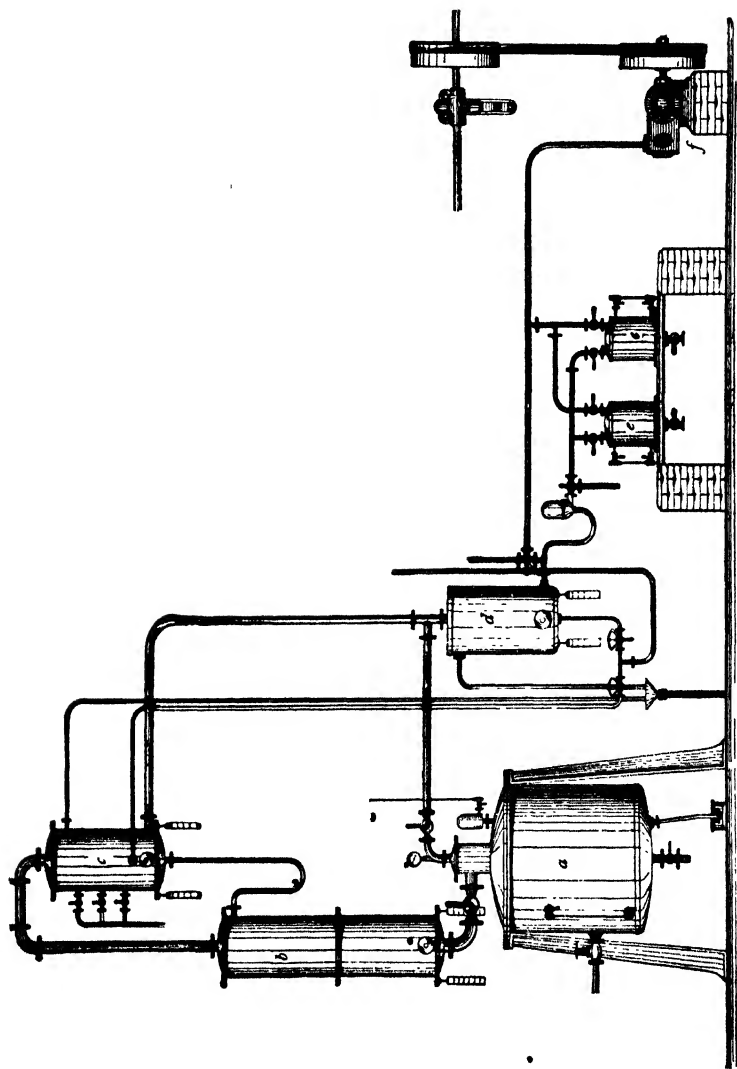


FIG. 49.—VACUUM DISTILLATION PLANT FOR REFINING WASHED TAR-FREE PINE OIL.
a, boiling vessel; *b*, column; *c*, dephlegmator; *d*, condenser; *e*, *e*, interchangeable receivers; *f*, vacuum pump.

unpleasant odour ; in fact,⁷ many people prefer the odour of refined pine-oil, which somewhat resembles that of lemon-oil.

The first runnings obtained during the steam distillation of crude pine-oil are refined in a similar manner, and those fractions which are still worth working up for pine-oil are mixed with the corresponding fractions obtained in the main process. The first runnings may also be combined with the last runnings to form a second-grade article.

It is useless to lay down definite instructions for the working-up of softwood-tar and tar-oils, since the mode of procedure will always depend on the possibility of disposing of the various products.

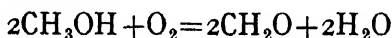
CHAPTER XVIII

FORMALDEHYDE

THIS substance was discovered by A. W. von Hoffmann in 1867. The original and very primitive process of manufacture was elaborated as a result of the investigations of Tollens, von Loew, Kablukow and Trillat. The researches of Tollens, especially, may be regarded as having rendered possible the manufacture of formaldehyde on a large scale.

The method of preparation is based on the oxidation of methyl alcohol by means of oxygen, atmospheric air being employed as the source of oxygen.

When methyl alcohol is mixed with air in the proportion indicated by the equation :



and the mixture is passed over some substance which acts as an oxygen carrier, the methyl alcohol is oxidised to formaldehyde.

This reaction does not take place at ordinary temperatures ; in practice, it is necessary to heat the substance acting as oxygen carrier or catalyst to about 300° C. before the mixture of methyl alcohol and air is admitted.

Hoffmann prepared formaldehyde originally by making use of this reaction, and even at the present day no other method of manufacture can compete with the original process.

Attempts have been made to manufacture formaldehyde by the oxidation of ethylene or methane with air or oxygen, and by the destructive distillation of salts of formic acid, but none of these processes has proved successful on the industrial scale.

According to the above equation 32·04 grams of methyl alcohol require 16 grams (11·2 litres) of oxygen at 0° C. and 760 mm. Since 11·2 litres of oxygen correspond to 53·33 litres of air, it follows that 100 grams of methyl alcohol (100 per cent) require 166·5 litres of air at 0° C. and 760 mm.

The volume of air required under different conditions of

temperature and pressure may be calculated from the following formula, where

t = temperature in centigrade degrees.

B = pressure in mm.

w = tension of water vapour present in the air at temperature t .

$$V \frac{t}{B} = \frac{x \times 760 \times (273 + t)}{(B - w) \times 273}$$

On applying this formula to air at about 15° C. and average pressure, it will be seen that at least 2 litres are necessary for the oxidation of 1 gram of methyl alcohol.

Experience has shown that a mixture of the above composition is useless for the production of formaldehyde from methyl alcohol, since in these conditions the reaction, which is entirely exothermic in character, proceeds much too violently and consequently takes quite a different direction from that shown by the above equation.

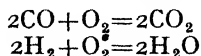
The investigations of Orloff¹ on the preparation and properties of formaldehyde, and more especially his examination and identification of the gases which are formed during the oxidation process, show that the main reaction is always accompanied by secondary reactions.

In the first place, methyl alcohol, in contact with the catalyst, becomes oxidised to formaldehyde according to the above equation.

The formaldehyde in passing over the hot catalyst then undergoes partial decomposition into carbon monoxide and hydrogen ;



The oxygen entering the process is not utilised completely for the formation of formaldehyde, and a sufficient amount remains to oxidise the carbon monoxide and hydrogen, resulting from the last reaction, to carbon dioxide and water respectively.



All these reactions are exothermic in character, consequently it is easy to account for the fact that the catalyst, after it is in

¹ Published in the Journal of the Russian Chemical Society. See also Journ. Chem. Soc. Abstracts, 1907, **92** [1] 892, 1008; 1908, **94** [1] 77, 761; and "Formaldehyd," von J. E. Orloff (translated into German by Dr. Carl Kietzbl), Leipzig, 1909, J. A. Barth.

full operation, assumes a comparatively high temperature. The higher the temperature of the catalyst, the greater is the tendency for secondary reactions to occur.

For the preparation of formaldehyde on really sound lines it is essential, therefore, that the oxidation process be carried out at a temperature which is just sufficient to ensure conversion of methyl alcohol into formaldehyde.

According to the investigations of Orloff the optimum temperature is about 300°C . Below this temperature the formation of formaldehyde diminishes considerably or ceases altogether; if this temperature is exceeded, the secondary reactions mentioned above take place to an increased extent, and the yield is correspondingly reduced.

Although the present author, who has been in close touch with the formaldehyde industry for many years, does not quite agree with these statements, he considers it necessary to quote them because Orloff was the first to study the conversion of methyl alcohol into formaldehyde from a purely scientific point of view.

Unfortunately, the methods adopted in these investigations, which were performed with only small quantities of methyl alcohol, cannot be translated into practice as they stand; nevertheless the work of Orloff has helped very decidedly to explain the process by which formaldehyde is formed.

As already mentioned, the composition of the air-alcohol mixture entering the process governs the reaction temperature of the catalyst, the conversion of methyl alcohol into formaldehyde, and the extent to which the secondary reactions occur.

Hence, the first necessity is to introduce into the process an air-alcohol mixture of absolutely uniform composition at a perfectly regular rate.

In the author's opinion, the method adopted by Tollens and Orloff to ensure these conditions is open to objection; the apparatus used by these two investigators certainly allows the supply of air to be regulated, but not that of the methyl alcohol.

Tollens and Orloff prepare the air-alcohol mixture by heating methyl alcohol in copper vessels, through which air is passed by suction or pressure. Obviously, the amount of alcohol which is vaporised in these conditions must vary

according to the amount of heat supplied ; in consequence—assuming that the air is supplied at a constant rate—the composition of the air-alcohol mixture must also vary. Moreover, the presence of considerable quantities of boiling methyl alcohol is always a source of danger owing to the possibility of fire or explosion.

The present author, in his patent process,¹ has succeeded in removing all objectionable features of the above nature by employing the air, which is preheated and supplied in measured quantities, to vaporise measured quantities of liquid methyl alcohol on the counter-current principle.

In this process, the amount of alcohol present in the mixing apparatus during a given period is never greater than that which must be supplied to the air entering the apparatus during the same period ; consequently, the composition of the mixture does not vary.

This method of preparing the air-alcohol mixture has proved extremely successful, and is used in a large number of formaldehyde factories.

The preparation of this mixture forms the first operation of the process. The methyl alcohol should show a concentration of at least 99 per cent, and at the most should not contain more than 0.5 per cent of acetone, practical experience having shown that if less pure alcohol is used the yield of formaldehyde diminishes. Apart from acetone, the alcohol should be as free as possible from the higher-boiling components of wood-naphtha, and more especially from inorganic matter such as chlorine ; the latter, according to statements in the literature, is occasionally found in methyl alcohol, and, even if present in only small traces, has an extremely injurious effect on the formaldehyde process.

Next in importance to the arrangements for preparing an air-alcohol mixture of uniform composition is the apparatus in which the oxidation of methyl alcohol is effected.

In its simplest form this section of the plant consists of a copper tube containing the catalyst. As catalysts, the following materials have been recommended : platinised asbestos, asbestos coated with copper, platinised coke, coke coated with copper, platinum or copper turnings and finally rolls of platinum or copper gauze. In practice, copper gauze has proved the most satisfactory of all these materials ; it is

¹ German patent, 106,495.

certainly superior to platinum and also to iron, which in this connection has little value as a catalyst.

Instead of a single tube several may be employed, thus giving to this section of the plant the form of a mitrailleuse.

The catalyst inside the tubes must be visible to the eye, and some device must also be provided for heating it to a dull red heat and thus initiating the process. Formerly, this was effected by surrounding the tubes with glowing charcoal or by bringing the flame of a benzine soldering lamp into contact with the catalyst; a very complicated and expensive system of electric heating was also employed, and another method consisted in placing platinum sponge in contact with the catalyst, on the same principle as the arrangement for lighting an Auer gas-burner. In the author's process, ignition is effected in a much simpler manner, the alcohol-air mixture itself being used for the purpose.

For a given performance the tubes must, of course, possess a certain definite free cross-sectional area; similarly, a definite surface-area of catalyst must be provided.

Any given rate of production of formaldehyde from methyl alcohol always corresponds to a definite amount of catalyst possessing a definite surface-area. If too much or too little of the catalyst is present, the yield is affected.

As soon as the air-alcohol mixture comes into contact with the catalyst—which has been heated previously to the proper temperature by one or other of the methods mentioned above—formation of formaldehyde sets in, as is indicated by the catalyst beginning to glow. The catalyst continues to glow throughout the process, as may be observed through mica windows let into the tubes, and no further supply of heat from outside is required; in fact, it is an advantage if the tubes are cooled to a certain extent, and for this reason the mitrailleuse type of apparatus is freely adopted, since it presents a large surface to the cooling action of the atmosphere.

Even if the air-alcohol mixture possesses the composition which experience has shown to be most suitable, and the weight and surface-area of the catalyst stand in correct relation to the amount of mixture introduced, it is never possible to carry the process of conversion so far that the 40 per cent formaldehyde of commerce results.

Formaldehyde is usually sold on a volume-percentage basis. A product of 40 per cent by volume is one which contains

40 kilos. of formaldehyde (100 per cent) in 100 litres. Since the specific gravity of this product (formalin) is 1.085-1.090, the formaldehyde content amounts to 36-36.5 per cent by weight. A product composed of about 36 per cent by weight of formaldehyde (100 per cent) and about 64 per cent of water cannot be preserved, since the formaldehyde gradually polymerises into diformaldehyde or triformaldehyde (trioxy-methylene), which renders the liquid turbid and reduces its value.

The best method of preventing polymerisation is to allow a certain amount of methyl alcohol to remain in the finished product. The amount necessary for this purpose varies from 33 to 40 per cent of the weight of formaldehyde (100 per cent), according to the season of the year and the atmospheric temperature. Commercial formalin therefore contains approximately:—

	Per cent.
Formaldehyde	36
Methyl alcohol	12
Water	52

As already mentioned, it is impossible to obtain a product of this concentration by the oxidation process, since the latter never proceeds quantitatively, a portion of the methyl alcohol always remaining unoxidised. The higher the proportion of methyl alcohol in the original mixture, and the lower the temperature of reaction below the optimum temperature, the greater is the amount of methyl alcohol remaining unchanged.

The mixture of vapour and gas leaving the catalyst consists of formaldehyde, water, methyl alcohol, small quantities of methylal, nitrogen, carbon dioxide, carbon monoxide, hydrogen, possibly some oxygen and, according to Orloff, a certain proportion of ethane.

The next task is to obtain a formaldehyde solution of the above composition from this mixture of reaction products. Formerly, this was carried out by passing the mixture of gas and vapour through condensers which separated the main bulk of the formaldehyde, water, unchanged methyl alcohol and methylal in the form of a liquid mixture. This product contained about 30 per cent of formaldehyde and in addition a considerable amount of methyl alcohol which it was necessary to recover: the mixture was therefore rectified in a column still which separated the excess of methyl alcohol,

and water was added to replace the latter. These operations do not offer the slightest difficulty, but they cannot be carried out without incurring considerable loss.

In view of this disadvantage, the author, who formerly employed the same method of concentrating the product, applied a process of fractional condensation to the mixture of gas and vapours leaving the reaction chamber, with the object of isolating formaldehyde in a suitable form and at the same time continuously separating the excess of methyl alcohol.

Tollens had already employed a similar method, but his process did not render it possible to remove the excess of methyl alcohol so effectively that the finished commercial product contained no more than the requisite amount of that component. It will be evident that the yield of formaldehyde must diminish and the cost of production increase, as the amount of methyl alcohol remaining in the finished product increases. By means of the author's process of fractional condensation—of which Orloff approves—it is possible to obtain a product containing any proportion of methyl alcohol. The process may be conducted in such a manner that formalin containing 36 per cent of formaldehyde (100 per cent) and 12 per cent of methyl alcohol is obtained directly from the apparatus; it is even possible to produce, if required, an article containing at least 40 per cent of formaldehyde and any proportion of methyl alcohol desired.

It will be readily understood that this section of the plant plays an important part in the process, and that the yield is partly dependent on its satisfactory operation.

The remaining products of the reaction are the non-condensable gases mentioned above—namely, nitrogen, carbon dioxide, carbon monoxide, hydrogen and ethane.

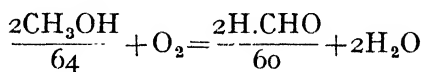
These gases cannot be allowed to escape into the atmosphere without further treatment, for in passing through the apparatus they have become saturated with methyl alcohol, which must be recovered if it is desired to carry out the process on strictly economic lines. The gases are therefore washed with water in a scrubber of suitable design; the methyl alcohol and any methylal present are extracted by the water to form a 20–30 per cent solution of methyl alcohol; this is worked up by intermittent or continuous rectification to the concentration at which the alcohol was originally employed—namely, 99 per cent—and the product is returned to the process.

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A formaldehyde plant consists of the following parts :—

1. The arrangement for supplying air at a constant rate.
2. The methyl alcohol vaporiser.
3. The arrangement for mixing the air and methyl alcohol.
4. The oxidation apparatus.
5. The arrangements for separating excess of methyl alcohol and condensing the finished product.
6. The arrangement for washing the waste gases.
7. The arrangement for concentrating the washings.

According to the equation—



it should be possible, theoretically, to obtain 195 kilos. of a solution containing 40 per cent by volume of formaldehyde, and possessing the composition given on page 372, from 100 kilos. of methyl alcohol.

This yield, however, is never obtained in practice, since the secondary reactions mentioned above always occur to some extent. The highest yield which the author ever obtained by his process was 175 kilos. of a 40 per cent solution from 100 kilos. of methyl alcohol (99 per cent)—that is, about 90 per cent of the theoretical yield. It must also be mentioned that this result was obtained in the course of an investigation in which the process was under the constant control of an experienced chemist.

If, as in normal circumstances, the running of the process must be left to an ordinary workman, with only occasional control by a chemist, it is impossible to obtain the above yield, which is equivalent to 175 per cent of the original amount of methyl alcohol employed. In normal conditions of practice the yield falls to 150–160 per cent. Apart from the skill of the operator, the yield also depends on the temperature of the cooling water, the purity of the air, and above all on the reliable operation of the arrangement which serves for the preparation of the alcohol-air mixture.

The process of manufacturing formaldehyde may appear to be simple; in reality it is not so, as long as the object is to produce such yields as will enable the product to be sold at competitive prices.

CHAPTER XIX

CONVERSION OF CHARCOAL INTO BRIQUETTES

STICK charcoal, obtained by the carbonisation of blockwood, can readily be sold without undergoing further treatment. Along with the stick charcoal, however, a certain amount of small waste or "breeze" is always obtained, chiefly as a result of the disintegration of larger pieces during the withdrawal of the charcoal from the retorts and its subsequent transport to other parts of the factory. Charcoal "breeze" is a much less valuable product than stick charcoal, and manufacturers have naturally attempted to convert the material into some form in which it will command a higher price. Further treatment of breeze charcoal is only profitable if carried out on a moderately large scale; consequently it is confined to the larger wood-distillation factories. Formerly, the usual method of utilising the "breeze" was to convert it into charcoal briquettes, which were used for heating railway carriages and living-rooms, and generally for all purposes which required a fuel capable of burning slowly without giving rise to smell, smoke or soot.

At one time these briquettes commanded a good price, often double that obtainable for ordinary coal, and consequently this manufacture proved quite a profitable business for certain wood-distillation factories which were also in a position to purchase "breeze" from other factories. Another source of raw material was the spirit industry, which at one time made use of large quantities of charcoal as a filtering medium. The charcoal used for this purpose was prepared by breaking up stick charcoal, screening the broken material to remove all pieces below a certain size, and igniting the remainder. This process resulted in the production of a considerable quantity of "smalls," which were unsaleable in that form, but could be utilised very satisfactorily as raw material for the manu-

facture of charcoal briquettes. As a rule, therefore, filter-charcoal and briquettes were manufactured side by side.

Owing to the improvements which have been effected in the construction of the plant used for refining spirit, as well as in the process of rectification, the use of filter-charcoal has greatly diminished; similarly, improvements in the method of heating railway carriages have gradually led to the displacement of the former primitive system—according to modern ideas—of heating with charcoal briquettes. To-day, the consumption of briquettes by the German railway companies does not amount to more than about 300 waggon loads per annum. Even on this modest scale the manufacture of briquettes was quite a profitable business, as long as it was still possible to obtain 12-13 shillings per 100 kilos. for the article; but it became unprofitable when the “Kasseler Trebertrocknungsgesellschaft,” which has been mentioned in previous chapters, put briquettes on the market at throw-away prices. The price fell to about 7s., or even less, per 100 kilos., a figure which represented very little profit to the manufacturers and did not compensate for the disagreeable nature of the process, which is an extremely dirty one. As is well known, the above Company endeavoured to find a really sound process for the carbonisation of small wood-waste, and believed that by the purchase of the Bergmann patents (see p. 172) this object had been achieved. A large number of factories were erected in rapid succession to work the Bergmann patents, but soon after the process was started up it was realised that the charcoal briquettes obtained from the previously briquetted shavings, etc. would not stand transport. The company was thus faced with a large quantity of charcoal “smalls” for which some method of utilisation had to be found. This form of charcoal appeared to be ideal raw material for the manufacture of railway briquettes; consequently, several factories were erected to deal with the material in this way, and naturally the result was a fall in the price of briquettes.

In manufacturing lignite—or coal—briquettes the powdered material is simply compressed, usually without the addition of any binding material, provided that the coal contains sufficient bituminous matter to meet the purpose. In making charcoal briquettes, however, certain materials are added, in particular, starch paste, which acts as a binding material, and sodium

nitrate, which acts as a source of oxygen, thus enabling the briquettes to fulfil their particular function, namely, to burn practically in the absence of air and without emitting any smoke or odour.

The manufacture of charcoal briquettes is carried out by pulverising the charcoal and then sorting out the larger particles on shaking-sieves. The sieved product is then transferred to fine-crushing mills, of which several different types are available. The fine powder is mixed with sodium nitrate and starch paste in special mixing appliances, and the mass is then conveyed to edge-runners in which it undergoes a final process of grinding and mixing.

After passing through roller-mills which loosen the material, the mixture is delivered to the presses in which the actual conversion into briquettes is effected. These presses vary greatly in size. The usual daily output is about 10,000 briquettes, each weighing 0.3-0.5 kilo. The pressed blocks are removed from the presses and placed on cars, which are then run into drying chambers. These cars are constructed of flat iron and are about $1\frac{1}{2}$ m. long, 1 m. wide and 1.3 m. high; they carry five trays made of wire-gauze or perforated sheet-iron on which the briquettes are carefully laid. The drying chambers consist of brickwork tunnels which are provided with a door at either end and are heated internally to a temperature of 50-70° C. by means of waste heat. Usually, several drying chambers are combined into one system, which makes it possible, by passing the cars through a series of chambers in succession, to start the process at a low temperature and to continue at gradually increasing temperatures until the final stage is reached. In order to facilitate the movement of the cars, rail-tracks fitted with turntables are laid down on both sides of the drying chambers. The chambers must be well ventilated, otherwise the drying process only goes on slowly owing to the accumulation of vapour. Since the charcoal frequently becomes ignited, it is necessary to keep the process under close observation, in order to prevent any danger of fire.

The finished briquettes are then tested, in order to ascertain, if they will burn for the required length of time and if the amount of ash lies within the specified limits. If the results are satisfactory, the briquettes are removed from the cars and packed directly into small boxes for despatch. The whole

installation is similar to that employed for briquetting coal and lignite, and the profits obtainable from the industry depend largely on the mechanical equipment of the factory.¹

¹ For a detailed description of briquetting plant see "A Handbook of Briquetting," by G. Franke. English translation by F. C. A. H. Lantsberry. (London, 1916, Charles Griffin and Co., Ltd.)

CHAPTER XX

ANALYTICAL SECTION

IN wood-distillation, as in all other branches of technical chemistry, analytical control of the process and systematic examination of the raw material and outgoing products have been followed by the best results. At one time, wood-distillation was carried out in a purely empirical manner without any scientific supervision; more recently, however, the pressure of competition has compelled manufacturers to devote the greatest possible attention to methods of production, and to supply products which are at least equal in quality to those of their competitors and at the same time are manufactured at minimum cost.

Owing to these conditions an opening for the work of the chemist was offered by the wood-distillation industry; that this work led to satisfactory results is proved by the fact that nowadays practically every factory possesses a laboratory and a staff of chemists.

The analytical operations which must be performed in connection with the process of wood-distillation comprise the examination of the raw materials and also of the intermediate and finished products.

A. Raw materials include :—

1. Wood.
2. Fuel.
3. Sulphuric acid.
4. Lime.

B. Intermediate and finished products include :—

- (a) Acetate of lime.
- (b) Pyroligneous acid.
- (c) Acetone.
- (d) Acetone oils.
- (e) Acetic acid

- (f) Crude wood-naphtha.
- (g) German denaturing wood-naphtha.
- (h) Austrian denaturing wood-naphtha.
- (i) English denaturing wood-naphtha.
- (k) French denaturing wood-naphtha.
- (l) American denaturing wood-naphtha.
- (m) Pure methyl alcohol.
- (n) Formaldehyde.
- (o) Wood-tar, tar-oils and pine-oil.
- (p) Charcoal.

A. EXAMINATION OF RAW MATERIALS

The chemical examination of the raw materials (included under A) need only be considered in so far as it necessitates the use of methods which ordinarily are not described in the textbooks of chemical analysis.

1. Wood. The wood derived from broad-leaved trees is composed of cellulose, lignin and water; that from coniferous trees of cellulose, lignin, rosin, terpenes and water.

In the destructive distillation of the wood, cellulose produces acetic acid, lignin the methyl alcohol, and rosin and terpenes the so-called pine-oil.

The moisture content of the wood exercises an important influence on the consumption of fuel, the performance of the plant and the yields.

For this reason, only air-dry wood—that is, wood containing approximately 20 per cent of moisture—should be carbonised.

In determining *moisture content*, a sufficient number of pieces to form a good average sample is selected from the batch of wood undergoing examination; transverse slices about 5 mm. thick are then cut from different parts of each piece, weighed, dried in an air bath at about 105° C. and weighed again, the operations being repeated until the weight is constant. The time required is usually ten hours.

The *rosin content* of coniferous wood is determined by extracting with ether or light benzine in a Soxhlet apparatus; it is assumed that the method of manipulating this apparatus is known.

Terpenes are determined by means of a steam-distillation. The wood is reduced to small pieces which are placed in an

autoclave, and a current of steam is then introduced. A pressure of 3 atm., or possibly rather more, is maintained in the apparatus. If present in sufficient quantity, the oil of turpentine, which is driven off in the form of vapour, forms a layer at the surface of the condensed distillate, from which it may be separated and its weight determined.

2. Fuel, and 3. Sulphuric Acid. These materials are examined by the ordinary methods given in the textbooks.

4. Quicklime (CaO) is used in wood-distillation chiefly to neutralise pyroligneous acid for the eventual production of grey acetate of lime. It is also used in smaller quantities for addition to wood-naphtha at various stages of the process of rectification (see p. 245).

The lime used for neutralisation must be as free as possible from impurities, especially magnesia; the latter causes a diminution in the weight of acetate of lime produced, since 1 part of acetic acid produces only about 1.18 parts of magnesium acetate as against about 1.31 parts of calcium acetate.

The presence of more than a small quantity of impurities insoluble in acetic acid, such as clay and sand, is also detrimental, since these substances cause loss by increasing the amount of filter-press sludge; moreover, a larger quantity of water is required to wash the sludge, with the result that the acetate liquor becomes diluted to an unnecessary extent and the costs of evaporation are increased accordingly.

The presence of any considerable amount of magnesia, or clay, may be recognised by the manner in which the lime slakes on treatment with water, since both these impurities give rise to a "lean" lime paste.

A rough estimation of the insoluble impurities may easily be made by dissolving a sample of the lime in dilute hydrochloric or acetic acid and noting the amount of residue.

After having made certain that coarser impurities are absent, it is usual to convert a portion of the lime into milk of lime by slaking it with a definite amount of water, and then to determine the density of the product by means of a Baumé hydrometer; with the aid of the table given below it is possible in this way to check the content of CaO .

Exactly 100 grams of quicklime are weighed out and slaked with water; as soon as the mass has crumbled into a soft paste it is washed into a litre flask which is then filled up to the mark.

After thorough shaking, the liquid is poured into a fairly

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wide glass cylinder, and the temperature is brought to 15° C. The hydrometer is introduced, and a reading is taken quickly before any deposit is formed.

MILK OF LIME TABLE

Degrees Baumé.	Weight of 1 litre. Grams.	CaO in 1 litre. Grams.	Degrees Baumé.	Weight of 1 litre. Grams.	CaO in 1 litre. Grams.
1	1007	7.5	16	1125	159
2	1014	16.5	17	1134	170
3	1022	26	18	1142	181
4	1029	36	19	1152	193
5	1037	46	20	1162	206
6	1045	56	21	1171	218
7	1052	65	22	1180	229
8	1060	75	23	1190	242
9	1067	84	24	1200	255
10	1075	94	25	1210	268
11	1083	104	26	1220	281
12	1091	115	27	1231	295
13	1100	126	28	1241	309
14	1108	137	29	1252	324
15	1116	148	30	1263	339

An impure lime is recognised with certainty by means of this test, which can be very rapidly carried out. Should it appear necessary, a closer examination may be made by the methods given in the textbooks.¹

B. ANALYSIS OF INTERMEDIATE AND FINISHED PRODUCTS

(a) Examination of Acetate of Lime.

In the wood-distillation factory, acetate of lime comes up for examination as a finished product; in the acetic acid and acetone factories, however, it constitutes a raw material which has been purchased as possessing a certain definite strength.

As mentioned previously, the main bulk of the acetate of

¹ See "Technical Methods of Chemical Analysis." Lunge and Keane, Vol. I, Part I, p. 482; Vol. I, Part II, p. 669. (London, 1908, Gurney and Jackson.)

lime employed for the manufacture of acetic acid and acetone is exported to Germany from America. The whole American output is in the hands of one organisation, at any rate as far as the sale of the product is concerned. In making contracts, a definite percentage content is naturally specified, amounting for American acetate of lime to 80–82 per cent of pure calcium acetate in a sample dried at 125° C. to constant weight; analysis by Stillwell and Gladding of New York establishes the figure for the American vendor.

This analysis is based on the distillation method of Fresenius, by which the total content of volatile fatty acids present in the acetate of lime may be determined satisfactorily.

Fresenius' method consists in decomposing acetate of lime with excess of phosphoric acid, distilling off the liberated volatile acids with steam, and determining the amount of acid in the distillate by titration with standard alkali.

For the purpose of analysis it is essential in the first place that a fair average sample of the acetate of lime be obtained. In the wood-distillation factory, sampling is quite a simple matter, since it is only necessary for a workman to take a number of small portions from each batch of the finished product as it is being filled into the sacks, and to place them in a large stoppered bottle which is kept ready for the purpose. Immediately after the batch is dispatched from the factory, the sample is analysed in the laboratory.

In the acetic acid and acetone factories, for which the acetate of lime is always purchased in sacks, the operation of sampling is much more difficult.

In these factories the acetate is usually stored in the sacks, which are only emptied when the contents are required for charging the plant. Since the period within which claims can be lodged against the vendor is limited, it is usually impossible to delay the analysis until the sacks are emptied; at the same time it is impracticable to open every sack for the purpose of securing a sample.

In these conditions the following procedure is adopted: A brass sampling tube of about 15 mm. internal diameter, sharpened at the end and fitted with a handle at the top like a cork-borer, is thrust through the side of the sack and well into the middle of the contents. The tube is then withdrawn, and the material contained in its lower portion is run into the sample-bottle. The sample must be taken from the middle of

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the sack, since the upper and lower parts may have been filled intentionally with superior material. The portions of the contents lying close to the sides of the sack are often damp owing to exposure to rain, etc., and therefore cannot be expected to furnish a fair average sample.

It is usual to take a sample from every fifth or every tenth sack, according to the amount of acetate in the consignment, all the samples being collected in one stoppered bottle. This bulk-sample must then be reduced to a homogeneous powder, for which purpose an ordinary iron pestle-and-mortar may be used, provided that the sample is not too large.

The apparatus required for the analysis by Fresenius' method consists of a glass retort of about 200 c.c. capacity, which rests with its neck sloping upwards on an ordinary wire gauze or, better, on an asbestos plate. The retort is heated by a Bunsen burner fitted with a rose-top, or else by a spirit lamp or petroleum burner. The neck of the retort is bent, at a convenient distance from the end, into an obtuse angle, the short limb of which is connected directly with a Liebig condenser. The tubulure of the retort is closed by a cork containing a delivery tube which is drawn out to a fine jet ending close to the bottom of the retort. The other end of the delivery tube is connected with a steam-generator by means of a rubber tube fitted with a screw-clip. The steam-generator may consist of a tin-can (an oilcan with a conical top is very suitable for the purpose) or a copper or glass flask; it is fitted as usual with a safety tube, about 2 metres high, which keeps the steam under slight pressure.

While the apparatus is being prepared, the water in the steam-generator may be heated up. As soon as everything is ready, the retort is disconnected, and a paper tube—made by rolling a sheet of paper round a cylindrical piece of wood—is inserted into the tubulure, with the object of preventing any of the acetate sticking to the glass while it is being introduced into the retort and thus possibly giving rise to loss.

Approximately 5 grams of the powdered sample of acetate are weighed out by means of a small hand-balance and introduced into a small aluminium boat of known weight. The exact weight of the contents of the boat is then determined, and as a rule will be found to differ by only a few centigrams from the first rough weight; hence, in performing

the analysis for purely factory purposes sufficiently accurate weighings may be made by using a sensitive hand-balance. The acetate is now introduced into the retort through the paper tube with the aid of a camel-hair brush, after which the boat and tube are washed with 50 c.c. of water. About 50 c.c. of pure phosphoric acid (sp. gr. 1.2) are then run into the retort by means of a pipette, care being taken that the acid does not come into contact with the tubulure; the retort is gently rotated for a short time and is then connected up again with the steam generator and condenser.

A 500 c.c. graduated flask is placed at the end of the condenser to act as a receiver and the retort is then heated cautiously—at first without introducing steam—since, at the outset, the contents of the flask are inclined to froth over.

When the distillate begins to come over, the heating may be carried on more rapidly, but the flame must be reduced again as soon as the residue shows signs of becoming viscous.

Careful heating is continued until the contents of the retort are just beginning to froth—an indication that nearly all the water has been evaporated. Steam is now passed in, but external heating is continued so as to prevent condensation. As soon as 500 c.c. have distilled over, the receiver is changed. As a precautionary measure, a further 100 c.c. is distilled over, but this portion is kept separate and titrated in one lot. A portion of the main distillate is tested for hydrochloric acid by adding silver nitrate and nitric acid; usually a slight cloud is obtained, but this small amount has no significance and may be overlooked. If the analyst has been present during the whole operation it is usually unnecessary to test the distillate for phosphoric acid; if he has only been able to give the operation occasional attention there is no certainty that some of the contents of the flask have not spurted over and the test should therefore be carried out.

If neither acid is present, 100 c.c. of the main distillate are titrated with *N*-sodium hydroxide, using phenolphthalein as indicator.

Since 1 c.c. *N*-sodium hydroxide = 0.079 gram calcium acetate the percentage of calcium acetate in the acetate of lime under examination

$$= \frac{n \times 0.079 \times 100 \times 5}{p}$$

where

n = the number of c.c. *N*-sodium hydroxide required for the 100 c.c. of distillate;

p = the weight of acetate of lime taken.

On titrating the second distillate (100 c.c.) in presence of phenolphthalein, it will usually be found that only one drop of *N*-sodium hydroxide is required, in which case the distillate may be neglected. If more is required the necessary corrections must be introduced into the above calculation.

Various modifications of this method of analysis are in use.¹

From the scientific point of view the method is not quite accurate, since the higher fatty acids are also titrated with the acetic acid; so far, however, no method has been devised by which the proportion of higher acids present can be estimated with certainty in the length of time at the disposal of a chemist in a wood-distillation factory.

The evaluation of sodium acetate, either in solid form or in solution, also the estimation of acetic acid in solutions of acetate of lime for the purpose of process control, are carried out in a perfectly analogous manner. When solutions are being analysed, however, it is unnecessary to introduce steam, as sufficient water is present. Only a single distillation in the presence of a suitable quantity of phosphoric acid is necessary.

For ascertaining the strength of solutions of the above salts in the course of the process the following tables are also useful. The data in each case refer to the *pure* anhydrous salts.

(b) Technical Analysis of Crude Pyroligneous Acid.

For purposes of process control, stock-taking, etc., it is necessary to determine the acetic acid and naphtha in the crude pyroligneous acid, though the latter is usually only an intermediate product. A small quantity of pyroligneous acid, however, comes on the market for pharmaceutical purposes, two different qualities being recognised by the German Pharmacopœia, namely:

1. *Crude Pyroligneous Acid* which must contain 6 per cent of acetic acid.

2. *Distilled Pyroligneous Acid* also containing 6 per cent of acetic acid.

¹ cf. Stillwell, *Journ. Soc. Chem. Ind.*, 1904, **23**, 305; Grosvenor, *Journ. Soc. Chem. Ind.*, 1904, **23**, 530; Fresenius and Grunhut, *Journ. Soc. Chem. Ind.*, 1908, **27**, 1012; Gladding, *Journ. Ind. Eng. Chem.*, 1909, **1**, 250; Jedlicka, *Zeit. Anal. Chem.*, 1910, **49**, 97; *Journ. Soc. Chem. Ind.*, 1910, **29**, 421; Munn, *Journ. Ind. Eng. Chem.*, 1918, **10**, 550; Pickett, *Journ. Ind. Eng. Chem.*, 1920, **12**, 570.

SPECIFIC GRAVITY AND CONCENTRATION OF SOLUTIONS OF
ACETATE OF LIME

Content of anhydrous calcium acetate. Per cent.	Sp. gr.	Content of anhydrous calcium acetate. Per cent.	Sp. gr.
1	1.0066	16	1.0708
2	1.0132	17	1.0750
3	1.0198	18	1.0792
4	1.0264	19	1.0834
5	1.0330	20	1.0874
6	1.0362	21	1.0925
7	1.0394	22	1.0996
8	1.0426	23	1.1027
9	1.0458	24	1.1078
10	1.0492	25	1.1130
11	1.0527	26	1.1189
12	1.0562	27	1.1248
13	1.0597	28	1.1307
14	1.0632	29	1.1366
15	1.0666	30	1.1426

SODIUM ACETATE

Content of anhydrous sodium acetate. Per cent.	Sp. gr.	Content of anhydrous sodium acetate. Per cent.	Sp. gr.
1	1.0058	16	1.0856
2	1.0116	17	1.0910
3	1.0174	18	1.0966
4	1.0232	19	1.1018
5	1.0292	20	1.1074
6	1.0341	21	1.1134
7	1.0390	22	1.1194
8	1.0439	23	1.1254
9	1.0488	24	1.1314
10	1.0538	25	1.1374
11	1.0591	26	1.1440
12	1.0644	27	1.1506
13	1.0697	28	1.1572
14	1.0750	29	1.1638
15	1.0802	30	1.1706

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Product (1) is obtained from crude pyroligneous acid by distilling off the naphtha and then adjusting the strength to 6 per cent of acetic acid by diluting with water.

Product (2) is obtained by driving off the naphtha from crude pyroligneous acid as for Product (1) and then distilling the residual acid. The distillate, which possesses a light yellow colour, is diluted with water to the required strength.

Direct Titration of Pyroligneous Acid. This operation is very easily carried out, provided that the acid is free from tar (Product 2), by titrating with *N*-sodium hydroxide in presence of phenolphthalein :

$$1 \text{ c.c. } N\text{-NaOH} = 0.06 \text{ g. CH}_3\text{COOH.}$$

With *distilled acid* the end point is very sharp, whereas with the *crude acid*, which contains tar in solution, it is impossible to obtain a reliable end point unless the acid has been highly diluted. Hence, before titrating crude pyroligneous acid the sample must be diluted with at least ten times its volume of water. 10 c.c. of the diluted liquor are then titrated, in this case with *N*/10-sodium hydroxide:—

$$1 \text{ c.c. } N/10\text{-NaOH} = 0.006 \text{ g. CH}_3\text{COOH.}$$

If the crude acid contains a high proportion of tarry matter it is usually impossible, even after tenfold dilution, to obtain a satisfactory result unless the spot method is used, since the action of sodium hydroxide on the tarry matter results in the formation of intensely coloured products. In this case the titration is again performed with *N*/10-sodium hydroxide, but the end point is detected by removing small drops of the solution and bringing them into contact with drops of phenolphthalein or with litmus paper.

In titrating crude pyroligneous acid directly with alkali not only the fatty acids but certain other components (phenols, etc.) are titrated at the same time; hence, if we calculate the total acidity as acetic acid, the resulting figures are too high.

Titration of Distilled Pyroligneous Acid. The only method of determining correctly the acetic acid or rather the sum of the volatile fatty acids in crude pyroligneous acid is to distil the acid first of all, thus eliminating the tarry matter, and then to titrate the distillate with standard alkali.

In this case most of the components which, in addition to the

volatile fatty acids, are capable of combining with alkalis, remain behind with the tar and are no longer included in the titration. 100 c.c. of crude pyroligneous acid are introduced into a retort or a fractionating flask which is connected with a Liebig condenser and is immersed in an oil bath containing a thermometer. The oil bath is gradually heated up to 140°C ., which is the end-temperature—measured in the residual tar—of the distillation on the large scale, and the pyroligneous acid is distilled into a 150 c.c. graduated flask, the heating being continued at 140°C . until nothing more passes over. The residue in the flask consists of about 10 c.c. of tar which, of course, still contains acetic acid. In order to drive over the last traces of acetic acid about 50 c.c. of water are added to the contents of the flask and distilled off completely into the first distillate, or, better, steam is passed through the residual tar, the oil bath being heated at the same time, until the distillate no longer contains any appreciable quantity of acetic acid.

The residue in the flask then represents the amount of tar which was present in solution in the pyroligneous acid.

The distillate is made up to 150 c.c., and 25 c.c. of this solution are titrated with *N*-sodium hydroxide.

If the above quantities are used, the number of grams of grey acetate of lime (80 per cent) which should be obtained from one litre of the pyroligneous acid $= n \times 5.9$ where n = number of c.c. of *N*-sodium hydroxide required.

Estimation of Wood-Naphtha in Crude Pyroligneous Acid.—For this determination a larger quantity—at least one litre—of the pyroligneous acid must be employed.

Exactly one litre of the crude pyroligneous acid is measured out into a round-bottomed glass flask or a copper flask of about 1.5 litres capacity, and approximately 50 per cent of the contents is distilled over on an oil bath. The distillate which contains all the naphtha is neutralised with thin lime paste, or, better, with caustic soda and again about 50 per cent is distilled off, with the object of further concentrating the naphtha. The second distillate, however, is still too weak to permit of its strength being determined with a reasonable degree of accuracy by an alcoholometric method; moreover, it contains methyl acetate which, owing to its relatively high specific gravity, would in any case render the result too low. The operation is therefore repeated as before

with addition of caustic soda, the volume of the distillate is measured at 15° C., and the specific gravity is then determined by means of a Mors or Westphal balance, a pyknometer or an accurate hydrometer; from the value obtained for the specific gravity the alcohol content is calculated with the aid of tables (see p. 455).

Assuming that at the end of three distillations 125 c.c. of distillate with a specific gravity of 0.9647 at 15° have been obtained, it will be found from the alcohol tables (see p. 455) that the distillate contains 23 per cent *by weight* of alcohol. The weight of the distillate must now be calculated by multiplying the volume by the specific gravity, thus, $125 \times 0.9647 = 120.58$ grams.

Since the distillate contains 23 per cent of alcohol, it follows that 1 litre of the pyroligneous acid contains $\frac{120.58 \times 23}{100} = 27.73$ grams of 100 per cent, or 34.66 grams of 80 per cent wood-naphtha.

If the third distillation is omitted, the resulting figure is too low by 10–15 per cent. In this estimation all the products associated with the methyl alcohol (acetone, acetaldehyde, allyl alcohol, etc.) are, of course, determined with the alcohol as wood-naphtha.

Estimation of Methyl Alcohol.—Should it be necessary to carry out a determination of methyl alcohol alone the method of Zeisel and Stritar ¹ is used. Ninety c.c. of filtered pyroligneous acid are neutralised with pure sodium carbonate in a 100 c.c. graduated flask and made up to 100 c.c. The solution is again filtered and 90 c.c. of the clear filtrate, after being rendered strongly alkaline, are then distilled from a 250 c.c. flask, until one-half the original volume has passed over; before the distillation, some fragments of porcelain and a few drops of liquid paraffin are added to the liquid to prevent bumping and frothing. (In carrying out the distillation Büttner and Wislicenus ² recommend the use of additional condensing apparatus which serves to prevent loss of the relatively low-boiling methyl alcohol.) The distillate is then treated with 0.5 gram of animal charcoal and filtered through a 9 cm. filter paper into a 100 c.c. flask. The flask which contained the distillate, and the filter paper, are washed repeatedly

¹ Zeit. anal. Chem., 1890, 29, 359; 1903, 42, 579; 1904, 43, 387, 394.

² Journ. prakt. Chem., 1909, 79, 177.

until the flask is nearly filled up to the mark. The liquid is then made up to 100 c.c. and thoroughly shaken.

Twenty-five c.c. of the liquid are then distilled with 10 c.c. of fuming, hydriodic acid (sp. gr. 1.7) in a Stritar apparatus,¹ a moderately rapid stream of carbon dioxide being passed through at the same time. The resulting methyl iodide vapour is led through a washing apparatus containing about 10 c.c. of water with 0.25–0.5 gram of red phosphorus in suspension, which absorbs any entrained hydriodic acid. After leaving the washing apparatus, the methyl iodide vapour passes into a solution of silver nitrate with which it reacts to form silver iodide. After 1–1½ hours, the liquid in the receivers remains clear above the precipitate—an indication that the process is finished.

The contents of the receivers are then washed into a fairly large beaker, treated with eight to ten times their volume of water, acidified with a few drops of nitric acid, and heated for about half an hour on a boiling water bath.

The precipitate of silver iodide is filtered off in an Allihn tube which contains a pad of asbestos. The tube is dried beforehand by heating it over a free flame and drawing air through it at the same time.

From the weight of silver iodide the percentage of methyl alcohol in the crude pyroligneous acid may be calculated.

According to Büttner and Wislicenus² very concordant results are obtained by this method.

In practice it is very rarely necessary to carry out this determination which is by no means simple. As a general rule there is no necessity to ascertain the content of pure methyl alcohol in the crude pyroligneous acid, but only the content of wood-naphtha, which represents the sum of the contents of methyl alcohol, acetone, etc.

For this purpose, simple distillation of the pyroligneous acid and evaluation of the distillate with the aid of methyl alcohol tables, as described above, are sufficient. In the experience of the author, the data obtained in this way agree quite well with the actual results of the large-scale process.

Estimation of Ketones.—The estimation of the individual ketones in pyroligneous acid, like that of methyl alcohol, is only of minor interest: of much greater importance is the

¹ Zeit. anal. Chem., 1903, 42, 579.

² Journ. prakt. Chem., 1909, 79, 183.

estimation of acetone together with other products which give the iodoform reaction.

The estimation of acetone is carried out by one of the methods described in connection with the testing of crude wood-spirit, especially the method of Messinger (see p. 422).

Another method is that of Deniges,¹ described in detail under "Crude Wood-spirit" (p. 424).

Büttner and Wislicenus² carry out Deniges' method in the following manner:—

The sample of pyroligneous acid is treated exactly as described above for the estimation of methyl alcohol by the Zeisel and Stritar method. Twenty-five c.c. of the distillate are treated with 10 c.c. of a 10 per cent solution of hydrogen peroxide and immediately afterwards with 25 c.c. of mercuric sulphate solution which is prepared by dissolving 5 grams of mercuric oxide in 100 c.c. of water to which 20 c.c. of concentrated sulphuric acid have been added. The mixture is then heated in a pressure flask on a water bath for ten minutes. After cooling, the precipitate is collected on a tared filter, dried at 90° C., and weighed. The dried precipitate corresponds to the formula: $2\text{HgSO}_4 \cdot 3\text{HgO} \cdot \text{CH}_3\text{COCH}_3$; by multiplying its weight by 0.0609, the weight of acetone in the 25 c.c. of distillate used for the estimation is obtained. It should be noted, however, that the precipitate also consists partly of similar double compounds formed by the higher ketones which in this method are calculated as acetone.

Estimation of Reducing Substances.—Besides acetic acid and its homologues, wood-naphtha, etc., the pyroligneous acid also contains considerable quantities of compounds which exhibit a reducing action, e.g. formic acid and aldehydes. These substances are estimated, according to the method of Büttner and Wislicenus, by reduction of standard ammoniacal silver nitrate solution.

Ten c.c. of pyroligneous acid (only 5 c.c. if the aldehyde content is high) are treated with 20 c.c. of concentrated ammonium hydroxide and 100 c.c. of *N*/10-silver nitrate, and the mixture is heated in a pressure flask on a boiling water bath for eight hours. After cooling, the contents of the flask are made up to 500 c.c., and the reduced silver is filtered off. The clear brownish-red filtrate is decolourised

¹ Compt. rend., 1898, 127, 963; Bull. Soc. Chim., 1899 [v], 19, 754.

² *Loc. cit.*

by treatment with animal charcoal for an hour, and subsequent filtration. The non-reduced silver in the colourless filtrate is determined by acidifying with nitric acid and titrating with ammonium thiocyanate, using iron alum as the indicator. The weight of silver which has been reduced is found by difference, and from this weight the content of reducing substances in the pyroligneous acid is calculated as acetaldehyde.

(c) Examination of Acetone.

As already mentioned in connection with the manufacture of acetone, the most important application of this product is in the preparation of certain kinds of military powder (cordite), for which purpose it must exhibit an exceptionally high degree of purity. It is also used in the celluloid industry, and to a certain extent in the organic chemical industry, e.g. in the manufacture of ionone, iodoform, and chloroform. As a rule, these industries are less strict in their requirements; it is true that they demand a very pure acetone, but usually it is unnecessary for the product to conform to the thirty-minute permanganate test of the British Government specification (see p. 395); persistence of colour for five minutes is sufficient, this being a guarantee that the product represents a highly rectified acetone.

The examination of acetone is carried out according to the specification issued by the German and Austrian powder factories, or, in cases where the product is intended for export to Great Britain, according to the British Government specification. Both methods of examination are given below. In neither case is any particular explanation necessary. Full details as to the manner in which Messinger's volumetric method of estimation and the determination of boiling points are carried out will be found in the sub-section dealing with the examination of wood-naphtha (p. 412).

Examination of Acetone according to the German Specification.¹

1. The acetone must be colourless and transparent. On evaporation it must leave no residue.
2. It must be miscible with distilled water in all proportions;

¹ See also "Chemisch-technische Untersuchungsmethoden," by Lunge and Berl, 7th Ed., Vol. II, page 1223. (Berlin, 1922, Julius Springer.)

the mixture must show no turbidity or precipitate, even after standing for a considerable time.

3. It must be absolutely neutral

Ten c.c. should not be coloured red by a few drops of phenolphthalein solution, but on adding 1 c.c. of *N*/10-sodium hydroxide a distinct red colouration should be produced. A solution of mercuric chloride should cause no turbidity when added to the acetone.

4. The acetone must show a strength of at least 98.5 per cent when measured with the thermo-alcoholometer at a temperature of 15° C.

5. The acetone should not contain more than 0.1 per cent of aldehyde and other easily oxidisable impurities. The aldehyde-content is estimated by reduction of a silver solution, which is prepared from 3 grams of crystallised silver nitrate, 3 grams of sodium hydroxide and 20 grams of ammonia (sp. gr. about 0.9) made up with water to 100 c.c. If kept in the dark this solution remains serviceable for a long period.

Ten c.c. of the acetone under examination are treated with 10 c.c. of distilled water and 2 c.c. of the above silver solution, covered up, and allowed to stand in the dark for half an hour. The liquid is decanted from the reduced silver and tested with a dilute solution of ammonium sulphide—as light coloured as possible—in order to ascertain if excess of silver is still present. The formation of a brownish-black precipitate, or a brown cloud, indicates that the liquid still contains silver and, therefore, that the aldehyde content of the acetone is less than 0.1 per cent.

6. On distillation at least 95 per cent of the acetone must pass over below 58° C.

7. The content of pure acetone as determined by the iodine method should not be less than 98 per cent.

This method of estimation is carried out in the following manner :—

Two grams of the acetone under examination are weighed out and diluted with water to 500 c.c. ; 10 c.c. of this solution are introduced into a glass flask and treated with 25 c.c. of *N*-sodium hydroxide ; 50 c.c. of *N*/10-iodine solution are then added, the mixture being shaken at the same time. The mixture is alternately shaken and allowed to stand for 15–20 minutes at 15° C., after which excess of *N*-sulphuric acid

(26 c.c.) is added in order to liberate the excess of iodine. The solution is then titrated with *N*/10-thiosulphate solution until the brown colour is discharged.

Since the end point is not quite sharp some starch solution is then added and any excess of thiosulphate present is determined by titrating with *N*/10-iodine solution.

The calculation of the acetone content is based on the fact that *one molecule of acetone* is converted into one molecule of iodoform by *six atoms of iodine*.

British Government Specification for Acetone.

1. The liquid is to be genuine acetone, and must contain no other ingredients except small quantities of substances which are normal by-products of the manufacture of acetone. It must be colourless and absolutely transparent, and when mixed with distilled water in any proportions it must show no turbidity. It must leave no residue on evaporation.

2. The specific gravity must not be greater than 0.800 at 15.5° C.
15.5° C.

3. The acetone must pass the prescribed potassium permanganate test by retaining its distinctive colour for not less than thirty minutes.

4. It must not contain more than 0.01 per cent of carbon dioxide and is to be otherwise neutral.

Note.—The acetone is to be tested within two days of use by the postassium permanganate test.

METHODS OF TESTING.

1. *Acidity, including Carbon Dioxide.*—50 c.c. of the acetone, diluted with an equal volume of water, are titrated with *N*/20-sodium hydroxide, using phenolphthalein as indicator.

Acidity, after Removal of Carbon Dioxide.—A further 50 c.c. of acetone, similarly diluted, are boiled until the bulk of the acetone has been removed and the liquid is titrated to phenolphthalein, using *N*/20-sodium hydroxide.

Alkalinity.—50 c.c. of the acetone, diluted as above, are titrated with *N*/20-sulphuric acid, using paranitrophenol as indicator.

2. *Potassium Permanganate Test.*—1 c.c. of 0.1 per cent solution of pure potassium permanganate in distilled water is added to 100 c.c. of the acetone, the liquid being maintained at 15.5° C.

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The *French* and *Belgian* specifications are similar. The acetone content must be at least 98 per cent. On distillation 95 per cent must pass over below 59° C.

(d) Examination of Acetone Oils according to the Swiss Specification.

The product to be supplied shall consist of 40–50 per cent of methyl ethyl ketone and 40–60 per cent of acetone oils.

Colour.—The product must possess a lemon-yellow colour and be absolutely clear.

Specific Gravity.—The specific gravity measured at 15° C. should be approximately 0.850

Boiling range.—The product should boil between 69° and 110° C. at a pressure of 760 mm. 500 c.c. are distilled in a copper Erlenmeyer flask of 1 litre capacity. Up to a temperature of 80° C. an Anderlini tube, about 50 cm. in length, is used as a rectifier; from 80° upwards a still head, 25 cm. in length with two bulbs, is employed for the purpose. The distillation must be regulated in such a manner that about 5–6 c.c. pass over per minute.

During this process the following amounts should distil over :—

Between 69– 75° C.	about 40–45 per cent.
„ 75– 80° C.	„ 10 per cent.
„ 80–150° C.	„ 35–40 per cent.
„ 150–180° C.	„ 10 per cent at the most.

Miscibility with Water.—The fraction obtained between 69° and 80° C. should be almost completely miscible with water.

Ten c.c. of the product are vigorously shaken with 40 c.c. of water in a graduated, stoppered cylinder, and allowed to stand for half an hour. A reading taken at 15° C. must show that at least 6.5 c.c. of the original 10 c.c. have been dissolved by the water.

Separation with Sodium Hydroxide.—On shaking 20 c.c. of the product with 30 c.c. of sodium hydroxide solution (sp. gr. 1.35), and allowing to stand for half an hour, not more than 1 c.c. should have been absorbed by the sodium hydroxide.

Absorption of Bromine.—2.447 grams of potassium bromate and 8.719 grams of potassium bromide are dissolved in a litre of water and 100 c.c. of this solution are treated with 20 c.c. of dilute sulphuric acid (1 in 3). For the permanent

decolourisation of the brown liquid obtained, not less than 4 c.c. of the acetone oils should be required.

Ketone Content.—The ketone content is estimated by the volumetric method of Messinger. Ten c.c. of the acetone oils are made up with water to 1 litre, 20 c.c. of the mixture are treated with 30 c.c. of 2 *N*-sodium hydroxide, and 75 c.c. of *N*/*s*-iodine solution are added drop by drop with constant shaking.

After standing for two hours the liquid is treated with 30 c.c. of sulphuric acid (100 grams in a litre), and the iodine which separates out is titrated with *N*/*10*-sodium thiosulphate solution. If *I* be the molecular weight of iodine, *A* the substituted molecular weight for the different ketones, *s* the specific gravity of these ketones, *N* the number of c.c. of *N*/*s*-iodine solution added and *n* the number of c.c. of thiosulphate used for the titration, then

$$\frac{\frac{A}{3I} (N - \frac{n}{2} \cdot 0.0254) \frac{100}{0.2}}{s} = \text{Percentage of ketones in the sample.}$$

The constant values in the above formula may be converted into a single factor which for the acetone oils = 1.55. On multiplying the number of c.c. of iodine solution which have entered into reaction, that is $(\frac{N}{s}) - n$, by this factor, the approximate percentage of ketones is obtained.

The acetone oils should show a ketone content of at least 90 per cent, as determined by the Messinger method and calculated according to the above formula.

Limit of Detection.—A 0.05 per cent aqueous solution of the acetone oils on treatment with a concentrated solution of phenylhydrazine hydrochloride (2 parts phenylhydrazine hydrochloride, 3 parts sodium acetate, 12–15 parts water), should still be rendered distinctly turbid.

(e) Analysis of Acetic Acid.

In describing the manufacture of acetic acid (Chap. XVI) it has been shown that three distinct grades are obtained in the course of the process, namely:—

1. Crude acetic acid.
2. Technical acetic acid.
3. Glacial acetic acid and vinegar essence.

Each of these products must undergo examination.

I. CRUDE ACETIC ACID.

The composition of this product varies, according to whether it has been manufactured by the hydrochloric acid process, the sulphuric acid process at ordinary pressure, or the sulphuric acid process under reduced pressure.

Crude Acetic Acid from the Hydrochloric Acid Process.

This product seldom reaches a concentration of more than 45 per cent and apart from small amounts of empyreumatic matter and the homologous acids, which are always estimated together with the acetic acid, it usually contains more or less hydrochloric acid.

The analysis is performed by weighing 20 grams of the acid into a 100 c.c. graduated flask on an ordinary tare balance (apothecary's balance) which is usually quite accurate up to 0.05 gram, making up with water to 100 c.c. and titrating 5 c.c. (1 gram of acid) with *N*-sodium hydroxide. Alternatively, 1 gram of the acid may be weighed into a stoppered weighing bottle on a chemical balance and then washed into an Erlenmeyer flask and titrated. If the diluted acid on treatment with silver nitrate (see p. 401) gives merely an opalescence and no precipitate, thus indicating the presence of only a negligible amount of hydrochloric acid, then the number of cubic centimetres of *N*-sodium hydroxide required for the titration of one gram of the acid may be referred directly to the tables on pages 407-410. The corresponding percentage by weight of acetic acid will be found in the second column of the table.

On the other hand, should the qualitative examination have indicated the presence of an appreciable amount of hydrochloric acid the latter must also be estimated. For this purpose a further 5 c.c. of the same dilute acid as was prepared for estimation with sodium hydroxide (see above) are neutralised with *N/2*-ammonia, which is more easily obtained free from chlorine than sodium hydroxide, no indicator being used. (The volume of *N/2*-ammonia which must be added is, of course, exactly double that of the *N*-sodium hydroxide required in the previous estimation.) The resulting solution of ammonium chloride is then titrated with *N/10* silver nitrate in the usual manner, using potassium chromate as the indicator.

If 1 gram of the crude acid is used for each titration and

a = number of c.c. of $N/10\text{-Ag.NO}_3$ required in Titration 2,

n = number of c.c. of $N\text{-NaOH}$ required in Titration 1,

then

$$\frac{n - \frac{a}{10}}{10} \times 0.06003 \times 100 = \text{true percentage by weight of acetic acid in the sample.}$$

Crude Acetic Acid from the Sulphuric Acid Process.—

This product is much more highly concentrated than that just considered. If the process is carried out under ordinary pressure the crude acid contains 72–75 per cent of acetic acid (exclusive of sulphurous acid); if the vacuum process is employed the product contains about 80 per cent of acetic acid and only traces of sulphurous acid.

Besides sulphurous acid, the crude acid also contains hydrogen sulphide and sulphuric acid. These impurities may be ignored since they are present only in very small traces which have no effect on the analysis. The sulphurous acid, however, must be estimated, and accordingly, the analysis comprises two operations, namely:—

1. Estimation of total acid by titration with N -sodium hydroxide.

2. Estimation of sulphurous acid by titration with $N/10$ -iodine.

For the latter estimation the acetic acid must be diluted until the concentration of sulphurous acid does not exceed 0.05 per cent.

In the first place 20 grams of the crude acid are weighed, as before, into a graduated flask, and made up to 100 c.c.; 5 c.c. of this solution (1 gram of crude acid) are then titrated with N -sodium hydroxide, using phenolphthalein as the indicator.

A further 5 c.c. (1 gram of crude acid) are diluted to 100 c.c., and 50 c.c. of this solution (0.5 gram of crude acid) are run into 10 c.c. of $N/10$ -iodine solution. (If the mixture is made by adding the iodine solution to the acid, the reaction will be incomplete.) The excess of iodine is then determined by titration with $N/10$ -thiosulphate.

If n = the number of c.c. of N -sodium hydroxide required

for 1 gram of the crude acid, and a = the number of c.c. of $N/10$ -iodine required for 0.5 gram of crude acid; then

$\left(n - \frac{2a}{10}\right) \times 0.06003 \times 100 = \text{true percentage by weight of acetic acid in the sample.}$

2. ANALYSIS OF TECHNICAL ACETIC ACID, GLACIAL ACETIC ACID AND VINEGAR ESSENCE.

The analysis of the actual commercial grades of acid, namely, technical acetic acid and chemically pure acetic acid is governed entirely by the requirements of the consumers.

As a rule only the acetic acid content and the residue on evaporation are estimated quantitatively. All other tests are qualitative in character and cover metals, salts, mineral acids and their salts, sulphurous acid and empyreumatic matter. These tests are carried out as follows:—

Qualitative Examination.

Inorganic Matter and Non-Volatile Organic Matter.—Fifty c.c. of the acid on evaporation should not leave more than 1 mg. of residue.

• *Arsenic.*—One c.c. of acetic acid, to which 3 c.c. of stannous chloride solution (prepared by saturating an aqueous solution of stannous chloride with gaseous hydrochloric acid) have been added, should show no brown colouration or precipitate on standing for an hour.

Instead of stannous chloride solution, which is usually coloured, Lunge recommends the use of a solution of sodium hypophosphite in hydrochloric acid (sp. gr. 1.19), which has been filtered through glass wool.

The Pharmacopœia Committee of the General Medical Council recommend the Gutzzeit test, as a limit-test for arsenic in acetic acid and other official substances. The method of carrying out this test is described in detail in the British Pharmacopœia.¹ The limit specified for acetic acid is two parts per million.

• *Sulphuric acid and sulphates* are detected by diluting

¹ "British Pharmacopœia," 1914 (London, Constable and Co., Ltd.), Appendix VI, p. 501. See also "Technical Methods of Chemical Analysis," Lunge and Keane, Vol. I, Part I, p. 374 (London, 1908, Gurney and Jackson).

5 c.c. of the acid with 100 c.c. of water and adding a few drops of barium nitrate solution.

Hydrochloric acid and chlorides can be detected by diluting 5 c.c. of the acid with 100 c.c. of water, acidifying with 5 c.c. of nitric acid and adding silver nitrate solution.

Metals.—A brown colouration or precipitate on passing hydrogen sulphide into the diluted acid, indicates the presence of lead, copper or tin. A further test for lead consists in diluting 5 c.c. of the acid with 25 c.c. of alcohol and adding dilute sulphuric acid: the lead if present is precipitated as sulphate.

Copper may also be detected by concentrating a portion of the acid to one-tenth of its original volume in a porcelain dish on the water bath, and adding excess of ammonia, which produces a blue colouration in presence of copper.

If the acetic acid is intended for edible purposes it must rigorously withstand these tests.

Empyreumatic Matter and Sulphurous Acid.—Apart from metallic impurities, acetic acid which is intended for the manufacture of vinegar must also be free from empyreumatic matter and sulphurous acid, since the presence of these impurities renders the flavour of the vinegar less agreeable. Empyreumatic matter can be detected by neutralising a sample of the acid with sodium carbonate and *smelling* the warmed liquid; also by diluting 1 c.c. of the acid with 30 c.c. of water and *tasting* the liquid; and finally by a chemical method which makes use of potassium permanganate.

In the trade great stress is laid on the permanganate test which is usually carried out as follows:—

Five c.c. of acetic acid are diluted with 15 c.c. of water and 3 c.c. of potassium permanganate solution (1:1000) are added. The red colour of the permanganate solution should persist for at least a quarter of an hour.

Sulphurous acid is detected by the decolourisation of iodide-starch paste, also by the precipitation of sulphur which occurs when the acid is mixed with a clear solution of hydrogen sulphide.

In addition to the above tests, the determination of certain physical constants—namely, boiling point, solidifying point and specific gravity—also serves to check the purity of the highly concentrated qualities of acetic acid.

The *boiling point* is determined in exactly the same manner

as described for wood-naphtha on page 428 ; for glacial acetic acid (95–99 per cent) it lies between 110° and 118° C.

Specific gravity and *solidifying point* are dealt with below (pp. 402–412).

An acid which complies with the above requirements and possesses the necessary concentration and correct boiling point will satisfy all consumers.

Quantitative Estimation.—Both the technical and the pure qualities of the acid found on the market consist essentially of acetic acid together with more or less water ; the technical qualities, however, contain in addition higher fatty acids, which are always reckoned as acetic acid. No other products are present, at any rate in the pure acid ; if present in the technical qualities, the amounts are so small that estimation is impracticable. The various qualities of acetic acid are therefore always sold on the basis of acetic acid content, assuming, of course, that they pass the qualitative tests as far as required.

The following methods are used for determining the acetic acid content :—

1. *Estimation by Specific Gravity.*—The specific gravity bears a perfectly definite relation to the acetic acid content, just as it does to the alcohol-content in mixtures of water and alcohol.

The specific gravity of the latter mixtures falls or rises as the alcohol-content increases or decreases : mixtures of acetic acid and water, however, do not exhibit the same regularity. On mixing concentrated acetic acid with water, contraction in volume takes place, and the specific gravity continues to increase and finally reaches a maximum, namely, 1.0748 at 15° C., when the mixture contains 77 per cent by weight of acid. This concentration corresponds to the hydrate $\text{CH}_3\text{COOH} + \text{H}_2\text{O}$. On further dilution with water, the specific gravity again decreases with the result that a 43 per cent acid has the same specific gravity as the 100 per cent acid, and a 51 per cent acid the same as a 97 per cent acid (see table on p. 404). Hence, when this method is used for determining the strength of an acid, and the specific gravity proves to be over 1.0553 at 15° , the acid must be diluted with water and a further measurement made. If, as a result of dilution, the specific gravity rises, the acid is stronger than 77 per cent ; if it falls, the acid is weaker than 77 per cent. Only after this

test has been carried out is it possible to ascertain the acetic acid content by reference to the table given on page 404.

Apart from this factor, which naturally renders this method of estimation somewhat complicated, another difficulty arises owing to the extremely small differences in specific gravity which are exhibited by acids of not very widely differing concentration, as will be seen on reference to the table. For example, the specific gravities of acids ranging from 72 to 84 per cent only differ in the fourth place of decimals, and then to a very small extent. These differences can only be recognised by employing scientific methods of measurement; even then, the correctness of the values obtained is somewhat doubtful. In dealing with the more highly concentrated qualities of acid (over 95 per cent) it is necessary to ascertain the *exact* percentage of acetic acid in order to arrive at the market value of the product. If it is desired to apply the specific gravity method, a Mohr balance or a pycnometer must be used, since it is impossible to obtain sufficiently accurate results by means of areometers. Consequently, the method is at least as lengthy as titration of the acid, which can always be relied upon to give correct results.

2. *Titration with Standard Alkali.*—This method is the one most generally used in practice. It consists in titrating a known weight or volume of the sample with *N*-sodium hydroxide, using phenolphthalein as the indicator. One c.c. of *N*-sodium hydroxide is equivalent to 0.06 gram of acetic acid.

For the *technical grades of acid* this estimation is carried out exactly as described for crude acetic acid (p. 398).

Twenty grams of the acid are weighed out on an apothecary's balance, and diluted to 100 c.c.; 5 c.c. of the dilute solution (1 gram of the original acid) are used for each titration.

The volume of *N*-sodium hydroxide used is then referred to the first column of the tables on pages 407-410, and the corresponding percentage content of acetic acid is found in the second column of the table.

For example, suppose 5 c.c. of the diluted acid (1 gram of the undiluted acid) require 14.40 c.c. of *N*-sodium hydroxide; then, according to the tables, the content of acetic acid in the sample amounts to 86.40 per cent by weight.

In so far as the titration is employed for process control, it may be left to the various operators, who will usually be found quite capable of performing it rapidly and accurately.

SPECIFIC GRAVITY OF ACETIC ACID AT VARIOUS TEMPERATURES (OUDEMANS)

Per cent.	Specific Gravity at			Per cent.	Specific Gravity at		
	12°	15°	20°		12°	15°	20°
0	0.9993	0.9992	0.9985	37	1.0511	1.0492	1.0458
1	1.0011	1.0007	0.9997	38	1.0522	1.0502	1.0468
2	1.0026	1.0022	1.0012	39	1.0533	1.0513	1.0478
3	1.0042	1.0037	1.0026	40	1.0543	1.0523	1.0488
4	1.0057	1.0052	1.0041	41	1.0553	1.0533	1.0498
5	1.0073	1.0067	1.0055	42	1.0564	1.0543	1.0507
6	1.0089	1.0083	1.0069	43	1.0574	1.0552	1.0516
7	1.0105	1.0098	1.0084	44	1.0583	1.0562	1.0525
8	1.0120	1.0113	1.0098	45	1.0593	1.0571	1.0534
9	1.0136	1.0127	1.0112	46	1.0602	1.0580	1.0543
10	1.0151	1.0142	1.0126	47	1.0612	1.0589	1.0551
11	1.0166	1.0157	1.0140	48	1.0621	1.0598	1.0559
12	1.0181	1.0171	1.0154	49	1.0629	1.0607	1.0567
13	1.0196	1.0185	1.0168	50	1.0638	1.0615	1.0575
14	1.0210	1.0200	1.0181	51	1.0647	1.0623	1.0583
15	1.0225	1.0214	1.0195	52	1.0655	1.0631	1.0590
16	1.0240	1.0228	1.0208	53	1.0663	1.0638	1.0597
17	1.0254	1.0242	1.0222	54	1.0671	1.0646	1.0604
18	1.0268	1.0256	1.0235	55	1.0678	1.0653	1.0611
19	1.0283	1.0270	1.0248	56	1.0685	1.0660	1.0618
20	1.0297	1.0284	1.0261	57	1.0692	1.0666	1.0624
21	1.0311	1.0298	1.0274	58	1.0698	1.0673	1.0630
22	1.0325	1.0311	1.0287	59	1.0705	1.0679	1.0636
23	1.0338	1.0324	1.0299	60	1.0711	1.0685	1.0642
24	1.0352	1.0337	1.0312	61	1.0717	1.0691	1.0648
25	1.0365	1.0350	1.0324	62	1.0723	1.0697	1.0653
26	1.0378	1.0363	1.0336	63	1.0729	1.0702	1.0658
27	1.0391	1.0375	1.0348	64	1.0734	1.0707	1.0663
28	1.0404	1.0388	1.0360	65	1.0739	1.0712	1.0667
29	1.0417	1.0400	1.0372	66	1.0744	1.0717	1.0671
30	1.0429	1.0412	1.0383	67	1.0749	1.0721	1.0675
31	1.0441	1.0424	1.0394	68	1.0753	1.0725	1.0679
32	1.0454	1.0436	1.0405	69	1.0757	1.0729	1.0683
33	1.0466	1.0447	1.0416	70	1.0761	1.0733	1.0686
34	1.0477	1.0459	1.0426	71	1.0765	1.0737	1.0689
35	1.0489	1.0470	1.0437	72	1.0768	1.0740	1.0691
36	1.0500	1.0481	1.0448	73	1.0771	1.0742	1.0693

Per cent.	Specific Gravity at			Per cent.	Specific Gravity at		
	12°	15°	20°		12°	15°	20°
74	1·0773	1·0744	1·0695	88	1·0758	1·0726	1·0674
75	1·0775	1·0746	1·0697	89	1·0752	1·0720	1·0668
76	1·0777	1·0747	1·0699	90	1·0745	1·0713	1·0660
77	1·0778	1·0748	1·0700	91	1·0737	1·0705	1·0652
78	1·0778	1·0748	1·0700	92	1·0728	1·0696	1·0643
79	1·0778	1·0748	1·0700	93	1·0718	1·0686	1·0632
80	1·0778	1·0748	1·0699	94	1·0706	1·0674	1·0620
81	1·0777	1·0747	1·0698	95	1·0792	1·0660	1·0606
82	1·0776	1·0746	1·0696	96	1·0644	1·0589
83	1·0775	1·0744	1·0694	97	1·0625	1·0570
84	1·0773	1·0742	1·0691	98	1·0604	1·0549
85	1·0770	1·0739	1·0688	99	1·0580	1·0525
86	1·0767	1·0736	1·0684	100	1·0553	1·0497
87	1·0763	1·0731	1·0679				

As mentioned above, in applying this method of estimation to the *highly concentrated grades of acid* it is necessary, owing to the degree of accuracy required, to weigh the acid on a chemical balance instead of an apothecary's balance. For this purpose a small stoppered bottle of about 50 c.c. capacity is counterpoised on the balance, and about 1 c.c. of acetic acid is carefully introduced from a pipette. The stopper is replaced, and the acid is weighed and then titrated with *N*-sodium hydroxide.

Since acetic acid is always purchased on the basis of percentage by weight, it is only permissible to use a *measured* quantity of the acid for titration if the specific gravity is known, in which case the figure derived from the titration can be corrected accordingly. Otherwise it is necessary to determine the specific gravity in addition to performing the titration, and, compared with direct weighing of the sample, no time is saved.

During the manufacture of acetic acid, however, numerous titrations must be made each day, and it is obvious that if the acid must be weighed in each case a considerable burden will be thrown on the chemist.

For this reason the author has prepared a set of tables (see pp. 407-410) which make it possible for the analyst

to use a *measured* quantity of acid for titration and at the same time to ascertain the percentage by weight directly from the volume of *N*-sodium hydroxide required. No weighing is necessary, and the operations are therefore comparatively simple.

If 1 c.c. of the acid instead of 1 gram is used for analysis, and the acetic acid content is calculated without taking the specific gravity into account, the result does not represent percentage by weight, but the number of grams of acetic acid present in 100 c.c. In this case the figures in the second column of the table represent *apparent* percentages by weight.

Corresponding to every *true* percentage by weight is a perfectly definite volume-weight percentage (that is, number of grams of acetic acid in 100 c.c.). For example, suppose that 100 grams of the acid in question contain 60 grams of absolute acetic acid; according to Oudemans' table (p. 404) 100 c.c. of the same acid will weigh 106.85 grams, and will contain

$$\frac{60 \times 106.85}{100} = 64.11 \text{ grams of absolute acetic acid.}$$

The method of using the following table requires little explanation. The figures in the first column represent the number of cubic centimetres of *N*-sodium hydroxide which may be required by 1 gram or 1 c.c. of the acid; the second column contains the corresponding *weight percentages*; and the third column contains the *volume-weight percentages* corresponding to *true* weight percentages. If 1 gram of the acid is used, the figures in the second column represent *true* weight percentages; if 1 c.c. is used, the figures represent *apparent* weight percentages.

For example, suppose that 1 gram of acetic acid requires 8.83 c.c. of *N*-sodium hydroxide; reference to Column 2 will show that the sample contains 53.00 per cent by weight of absolute acetic acid. On the other hand, suppose that 1 c.c. of the sample was used and again 8.83 c.c. of *N*-sodium hydroxide were required: in this case the figure 53.00 represents only the apparent weight percentage or volume-weight percentage. This figure must now be located in the list of volume-weight percentages in Column 3, and referred back to the figure on the same line in Column 2 representing the corresponding *true* percentage by weight, in this case about 50 per cent.

In carrying out the estimation, either a 1 c.c. pipette is employed, or else 10 c.c. of the sample are diluted to 100 c.c., and 10 c.c. of this solution (corresponding to 1 c.c. of undiluted acid) used for titration. The former method involves very precise measurement, and the temperature must be kept strictly at 15° C., consequently it is not very suitable from the practical point of view.

By diluting the acid, however, the errors of measurement and temperature are rendered smaller, so that even a workman is able rapidly to perform the analyses required for process control, and with the aid of the tables to obtain reliable data.

TABLES FOR CALCULATING THE PERCENTAGE BY WEIGHT OF ABSOLUTE ACETIC ACID FROM THE VOLUME OF *N*-SODIUM HYDROXIDE REQUIRED BY 1 GRAM OR 1 C.C. OF A SAMPLE OF ACETIC ACID

c.c. of <i>N</i> -sodium hydroxide required for 1 gram or 1 c.c. of acetic acid.	True weight percentages when 1 gram of acetic acid is used.	Volume-weight percentages corresponding to <i>true</i> weight percentages in Column 2.	c.c. of <i>N</i> -sodium hydroxide required for 1 gram or 1 c.c. of acetic acid.	True weight percentages when 1 gram of acetic acid is used.	Volume-weight percentages corresponding to <i>true</i> weight percentages in Column 2.
16.66	99.96	105.53	15.50	93.00	99.37
.61	99.66	—	.40	92.40	—
.56	99.36	—	.32	92.00	98.40
.51	99.06	104.74	.30	91.80	—
.46	98.76	—	.20	91.20	—
.41	98.46	—	.16	91.00	97.41
.36	98.16	—	.10	90.60	—
.31	97.86	103.92	15.00	90.00	96.41
.26	97.56	—	14.90	89.40	—
.21	97.26	—	.83	89.00	95.40
.16	96.96	103.06	.80	88.80	—
.10	96.66	—	.70	88.20	—
16.00	96.00	102.18	.65	88.00	94.38
15.90	95.40	—	.60	87.60	—
.83	95.00	101.27	.50	87.00	93.35
.80	94.80	—	.40	86.40	—
.70	94.20	—	.32	86.00	92.32
.65	94.00	100.34	.30	85.80	—
.60	93.60	—	.20	85.20	—

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c.c. of <i>N</i> -sodium hydroxide required for 1 gram or 1 c.c. of acetic acid.	True weight percentages when 1 gram of acetic acid is used.	Volume-weight percentages corresponding to <i>true</i> weight percentages in Column 2.	c.c. of <i>N</i> -sodium hydroxide required for 1 gram or 1 c.c. of acetic acid.	True weight percentages when 1 gram of acetic acid is used.	Volume-weight percentages corresponding to <i>true</i> weight percentages in Column 2.
14.16	85.00	91.28	11.40	68.40	—
.10	84.60	—	.32	68.00	72.93
14.00	84.00	90.23	.30	67.80	—
13.90	83.40	—	.20	67.20	—
.83	83.00	89.17	.16	67.00	71.83
.80	82.80	—	.10	66.60	—
.70	82.20	—	11.00	66.00	70.73
.65	82.00	88.11	10.90	65.40	—
.60	81.60	—	.83	65.00	69.62
.50	81.00	87.05	.80	64.80	—
.40	80.40	—	.70	64.20	—
.32	80.00	85.98	.65	64.00	68.52
.30	79.80	—	.60	63.60	—
.20	79.20	—	.50	63.00	67.42
.16	79.00	84.90	.40	62.40	—
.10	78.60	—	.32	62.00	66.32
13.00	78.00	83.83	.30	61.80	—
12.90	77.40	—	.20	61.20	—
.83	77.00	82.75	.16	61.00	65.21
.80	76.80	—	.10	60.60	—
.70	76.20	—	10.00	60.00	64.11
.65	76.00	81.67	9.90	59.40	—
.60	75.60	—	.83	59.00	63.00
.50	75.00	80.59	.80	58.80	—
.40	74.40	—	.70	58.20	—
.32	74.00	79.50	.65	58.00	61.90
.30	73.80	—	.60	57.60	—
.20	73.20	—	.50	57.00	60.80
.16	73.00	78.44	.40	56.40	—
.10	72.60	—	.32	56.00	59.70
12.00	72.00	77.32	.30	55.80	—
11.90	71.40	—	.20	55.20	—
.83	71.00	76.23	.16	55.00	58.59
.80	70.80	—	.10	54.60	—
.70	70.20	—	9.00	54.00	57.49
.65	70.00	75.13	8.90	53.40	—
.60	69.60	—	.83	53.00	56.38
.50	69.00	74.03	.80	52.80	—

c.c. of <i>N</i> -sodium hydroxide required for 1 gram or 1 c.c. of acetic acid.	True weight percentages when 1 gram of acetic acid is used.	Volume-weight percentages corresponding to <i>true</i> weight percentages in Column 2.	c.c. of <i>N</i> -sodium hydroxide required for 1 gram or 1 c.c. of acetic acid.	True weight percentages when 1 gram of acetic acid is used.	Volume-weight percentages corresponding to <i>true</i> weight percentages in Column 2.
8.70	52.20	—	6.00	36.00	37.73
.65	52.00	55.28	5.90	35.40	—
.60	51.60	—	.83	35.00	36.64
.50	51.00	54.18	.80	34.80	—
.40	50.40	—	.70	34.20	—
.32	50.00	53.07	.65	34.00	35.56
.30	49.80	—	.60	33.60	—
.20	49.20	—	.50	33.00	34.37
.16	49.00	51.97	.40	32.40	—
.10	48.60	—	.32	32.00	33.39
8.00	48.00	50.87	.30	31.80	—
7.90	47.40	—	.20	31.20	32.31
.83	47.00	49.76	.16	31.00	—
.80	46.80	—	.10	30.60	31.23
.70	46.20	—	5.00	30.00	—
.65	46.00	48.66	4.90	29.40	—
.60	45.60	—	.82	29.00	30.16
.50	45.00	47.56	.80	28.80	—
.40	44.40	—	.70	28.20	—
.32	44.00	46.47	.65	28.00	28.92
.30	43.80	—	.60	27.60	—
.20	43.20	—	.50	27.00	27.91
.16	43.00	45.37	.40	26.40	—
.10	42.60	—	.32	26.00	26.94
7.00	42.00	44.28	.30	25.80	—
6.90	41.40	—	.20	25.20	—
.83	41.00	43.26	.16	25.00	25.87
.80	40.80	—	.10	24.60	—
.70	40.20	—	4.00	24.00	24.81
.65	40.00	42.09	3.90	23.40	—
.60	39.60	—	.83	23.00	23.74
.50	39.00	41.00	.80	22.80	—
.40	38.40	—	.70	22.20	—
.32	38.00	39.90	.65	22.00	22.68
.30	37.80	—	.60	21.60	—
.20	37.20	—	.50	21.00	21.62
.16	37.00	38.82	.40	20.40	—
.10	36.60	—	.32	20.00	20.57

c.c. of <i>N</i> -sodium hydroxide required for 1 gram or 1 c.c. of acetic acid.	True weight percentages when 1 gram of acetic acid is used.	Volume-weight percentages corresponding to <i>true</i> weight percentages in Column 2.	c.c. of <i>N</i> -sodium hydroxide required for 1 gram or 1 c.c. of acetic acid.	True weight percentages when 1 gram of acetic acid is used.	Volume-weight percentages corresponding to <i>true</i> weight percentages in Column 2.
3.30	19.80	—	1.60	9.60	—
.20	19.20	—	.50	9.00	9.11
.16	19.00	19.51	.40	8.40	—
.10	18.60	—	.32	8.00	8.00
3.00	18.00	18.46	.30	7.80	—
2.90	17.40	—	.20	7.20	—
.83	17.00	17.41	.16	7.00	7.07
.80	16.80	—	.10	6.60	—
.70	16.20	—	1.00	6.00	6.05
.65	16.00	16.36	0.90	5.40	—
.60	15.60	—	.83	5.00	5.03
.50	15.00	15.32	.80	4.80	—
.40	14.40	—	.70	4.20	—
.32	14.00	14.28	.64	4.00	4.02
.30	13.80	—	.60	3.60	—
.20	13.20	—	.50	3.00	3.01
.16	13.00	13.24	.40	2.40	—
.10	12.60	—	.32	2.00	1.004
2.00	12.00	12.20	.30	1.80	—
1.90	11.40	—	.20	1.20	—
.82	11.00	11.17	.16	1.00	1.007
.80	10.80	—	.10	0.60	—
.70	10.20	—	0.05	0.30	—
.66	10.00	10.14			

In checking the strength of the product before it is despatched from the factory, the above method of estimation is always employed. The portions for analysis are either weighed out on a chemical balance, or else carefully measured out at 15° C., and the strength is ascertained by using the tables as explained above.

Besides the above methods of estimation, certain tests are available for determining approximately the strength of the more highly concentrated grades of acetic acid. The following may be mentioned:—

Estimation by means of Essential Oils.—This method is based on the property possessed by highly concentrated

acetic acid of dissolving essential oils. It is useful in checking the strength of the commercial glacial acetic acid, which should contain at least 97 per cent of absolute acid. One volume of the sample is agitated with nine volumes of oil of turpentine. If the strength is not less than 97 per cent, the liquids are completely miscible. Samples containing 99.5 per cent of absolute acid are miscible with oil of turpentine in all proportions. Oil of lemon, if freshly distilled, may be used in place of oil of turpentine.¹

Miscibility with Carbon Disulphide.—A very delicate test for water is to treat a sample of the acid in a dry test-tube with an equal volume of carbon disulphide, and warm the mixture in the hand for a few minutes. The liquid becomes turbid if any water is present in the sample.²

Determination of the Solidifying Point.—This method of estimating small amounts of water in acetic acid is used occasionally. Pure acetic acid solidifies at 16–16.5° C.; diluted acetic acid solidifies at lower temperatures, according to the amount of water present.

Rüdorff³ has ascertained the relations between content of absolute acetic acid and solidifying point; these relations are shown in the table on page 412.

In carrying out the determination of the solidifying point, a layer of acetic acid, 2–3 cm. in depth, is introduced into a specially thin-walled test-tube; a thermometer is then inserted, care being taken that it does not touch the wall of the tube at any point and that the bulb is completely immersed in the acid. The tube is suspended in a beaker which contains a suitable cooling agent (cold water or a mixture of water and ice). The acid tends to become supercooled, and solidification is often only induced by shock, and then takes place suddenly. When solidification sets in, the thermometer remains stationary for a short time, or it may rise slightly, in which case the highest point reached is taken as the solidifying point.

This method of estimation is much more complicated and delicate than the titration method, and is therefore more suitable for scientific work than for process control and examination of commercial products.

¹ Cf. *Bardy*, Chem. News, 1879, 40, 78.

² Allen's "Commercial Organic Analysis," Vol. I, p. 494 (London, 1909, J. and A. Churchill).

³ Pharm. Journ. [3], 1872, 2, 241.

SOLIDIFYING POINTS OF ACETIC ACID

Water to 100 parts of real acetic acid.	Water contained in 100 parts of the mixture.	Solidifying point ° C.
0.0	0.000	+ 16.7
0.5	0.497	+ 15.65
1.0	0.980	+ 14.80
1.5	1.477	+ 14.0
2.0	1.961	+ 13.25
3.0	2.912	+ 11.95
4.0	3.846	+ 10.50
5.0	4.761	+ 9.4
6.0	5.660	+ 8.2
7.0	6.542	+ 7.1
8.0	7.407	+ 6.25
9.0	8.257	+ 5.3
10.0	9.090	+ 4.3
11.0	9.910	+ 3.6
12.0	10.774	+ 2.7
15.0	13.043	— 0.2
18.0	15.324	— 2.6
21.0	17.355	— 5.1
24.0	19.354	— 7.4

(f) Analysis of the Various Grades of Wood-Naphtha.

CRUDE WOOD-NAPHTHA.

As already mentioned in an earlier chapter, it is unusual for the smaller wood-distillation factories to work up wood-naphtha into refined products; as a general rule these factories simply concentrate the product to about 80 per cent Tralles, and then put it on the market. These conditions apply in Germany, America and Austria-Hungary.¹ The extent to which this product must be examined differs according to whether the party concerned is the vendor or the purchaser and refiner of the crude wood-naphtha.

¹ In England, however, it is usual, even in the smallest factories, to work up the naphtha as far as possible into denaturing wood-spirit conforming to the British Government specification (see p. 432).

On the part of the vendor only a very simple examination of the product is necessary, since, having manufactured it himself, he has no need to look for foreign ingredients or to ascertain if a portion of the "middle runnings" has already been removed; in short, the vendor has only to take care that, in his own and the purchaser's interest, the declaration as to concentration in the invoice is correct, and that the crude product satisfies the few requirements in respect of quality (miscibility with water, etc.).

1. Alcoholometry of Wood-Naphtha.—In Germany, the crude wood-naphtha trade has adopted the same unit as is employed in the spirit industry to express the value of a liquid containing alcohol, namely, "litre per cent"; consequently the same type of measuring instrument—the so-called "thermo-alcoholometer"—may also be employed.

One litre per cent signifies the volume of absolute alcohol which is contained in a litre of 1 per cent alcohol, that is, 10 c.c. Hence 100 litres of 1 per cent alcohol, 50 litres of 2 per cent and 25 litres of 4 per cent all contain 100 litre per cent; similarly 1 litre of 90 per cent alcohol contains 90 litre per cent.

In practice it is usual to employ the larger unit, namely, "10,000 litre per cent," which is equivalent to 100 litres of absolute alcohol.

For American and Canadian wood-naphtha the commercial unit is the Wine gallon (3.785 litres) or the Imperial gallon (4.546 litres), containing 82 per cent by volume of wood-naphtha. The product is also sold on a weight-percentage basis.

As mentioned above, the strength of wood-naphtha is ascertained by means of an alcoholometer. In Germany the principal forms in use are *Richter's* alcoholometer, which indicates percentage by weight, and *Tralles'* alcoholometer, which indicates percentage by volume.

"Percentage by weight," as indicated by the alcoholometer, signifies the number of kilos. of 100 per cent alcohol contained in 100 kilos. of the product under examination.

"Percentage by volume" signifies the number of litres of 100 per cent alcohol contained in 100 litres of the product.

To convert percentage by volume (V) into percentage by weight (W), the value for the former is multiplied by 0.794

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(sp. gr. of absolute alcohol) and the figure so obtained is divided by the specific gravity (D) of the liquid :-

$$W = \frac{V \times 0.794}{D}$$

Previous to 1887 the Tralles alcoholometer was used in Germany for revenue purposes, but a system of weight alcoholometry is now employed. The official alcoholometers are made of glass and are graduated to show percentages of alcohol by weight at 15° C.

In France, Gay Lussac's volume alcoholometer is used. The readings on a Gay Lussac alcoholometer at 12° C. are almost identical with readings on Tralles' instrument at 15° C.

Unfortunately, Baumé's and Beck's hydrometers, Cartier's areometer, and other instruments calibrated in arbitrary "degrees" are still frequently used for assaying spirit. Tables are available by means of which the indications on any one of these instruments can be converted into degrees of any other¹; or the specific gravities corresponding to these "degrees" may be found in a chemical reference book,² and referred to alcohol tables which give the corresponding percentages of alcohol by weight and volume.

The system of alcoholometry used in Great Britain is more complicated. The standard of strength is termed "proof." Spirit of proof strength is defined as "that which at a temperature of 51° F. (10.6° C.) weighs exactly $\frac{1}{18}$ ths of an equal measure of distilled water" also at 51° F. "Proof spirit" has a specific gravity of 0.91976 at 15.6°/15.6° C. and contains 49.28 per cent by weight and 57.10 per cent by volume of anhydrous alcohol. A weaker spirit is said to be "under proof" (U.P.) and a stronger spirit "over proof" (O.P.).

"Sixty over proof" signifies that 100 volumes at 50° F. of the spirit in question, when diluted with 60 volumes of water, will produce 160 volumes of "proof spirit" at the same temperature. On the other hand, "60 under proof" indicates a spirit of which 100 volumes at 50° F. contain 40 volumes of "proof spirit."

¹ Cf. "Alcoholometric Tables," by Sir E. Thorpe (London, 1915, Longmans, Green and Co.). Tables II and III give the percentage of British Proof Spirit which corresponds to the indications on the various instruments mentioned above. Knowing this value, the percentages of alcohol by weight and volume can be ascertained from Table I.

² See "Chemiker-Kalender" (Berlin, Julius Springer).

The instrument used in Great Britain and most of the British Colonies for ascertaining the strength of spirits for revenue purposes is Sikes' hydrometer. No matter which of the above systems is employed, it is always necessary to have at hand an accurate set of tables which show the percentage of alcohol by weight and by volume corresponding to different specific gravities.

A large number of such tables is available, probably the most complete and reliable being the official tables prepared by Windisch.¹

All these tables refer to mixtures of ethyl alcohol and water. Although it is quite common practice to use them for ascertaining the strength of methyl alcohol mixtures it should be noted that serious errors may be introduced, since the specific gravity of aqueous methyl alcohol may differ considerably from that of aqueous ethyl alcohol of the same strength, especially between 10 and 40 per cent.

Tables for mixtures of water and methyl alcohol were drawn up by Dittmar and Fawsitt.² These tables have since been recalculated by Klason and Norlin.³ A later set of tables is that given by Doroschewski and Roshdestwenski⁴ and reproduced on p. 455.

The various alcoholometers in use are calibrated for a particular temperature, usually 15° C. In practice it is difficult, of course, to insist that the measurement shall always be made at that temperature; therefore, in order to enable the operator to use the instrument at other temperatures, its lower portion is constructed as a thermometer.

For purposes of process control an alcoholometer indicating percentage of alcohol by weight is used. The figure representing the *apparent* strength, together with the temperature at which it was obtained, is entered in a book by the operator. This book is sent periodically to the laboratory, where, by means of tables which are available for most of the different types of

¹ Published by Julius Springer, Berlin. For British factories which require to ascertain the strength of their products in terms of "proof" Thorpe's "Alcoholometric Tables" will be found most convenient (see footnote p. 414).

² Trans. Roy. Soc. Edin., 1889, **33**, ii, 509.

³ Archiv. Kem. Min. Geol., 1907, **2**, No. 27. See also Allen's "Commercial Organic Analysis," 4th Ed., 1909, Vol. I, p. 86.

⁴ Journ. Russ. Phys. Chem. Soc., 1909, **41**, 154. See also Journ. Soc. Chem. Ind., 1910, **29**, 173.

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instrument in use, the *apparent* strength is converted into *true* strength, that is, percentage by weight at 15° C.

The method of using the alcoholometer is very simple. The wood-spirit to be tested is introduced by means of a dipping-bottle or a siphon into a tall glass cylinder with an internal diameter of at least 40 mm. Before use, the cylinder must be absolutely dry, otherwise it must be rinsed out several times with the wood-spirit. Care must also be taken not to fill the cylinder to such a level that the liquid overflows when the alcoholometer is introduced. The instrument is then immersed in the liquid, but the reading is only taken when the thermometer is stationary, indicating that the temperatures of the cylinder, liquid and instrument have become equalised. (These temperatures usually differ, especially in winter). Having ascertained that the instrument is floating freely without touching the wall of the cylinder, the graduation coinciding with the surface of the liquid is read, care being taken to avoid parallax.

In dealing with finished products the *apparent* strength obtained in this way is converted into the *true* strength by means of the tables, and from this figure and the net weight of the consignment the number of commercial units—litre per cent, proof gallons, etc.—may be calculated for statement in the invoice. Before filling the containers in which the product is shipped, an average sample is taken and preserved until the period within which claims may be made in respect of the consignment has expired.

At first sight it may appear that if tables referring to ethyl alcohol are used, the figures obtained by the above method for the strength of crude wood-spirit can bear very little relation to the actual quality of the product. The only information which the determination furnishes is that the liquid consists, not merely of water, but of a mixture of water and certain other completely miscible components; also, that a certain percentage by weight of these components, taken in the aggregate, is present, assuming of course that each individual component possesses the same specific gravity as ethyl alcohol and exhibits the same degree of contraction on admixture with water.

On considering the specific gravities of the more important components of crude wood-spirit we find that the values for methyl alcohol and acetone approach very closely to that

for ethyl alcohol, and from a practical point of view the deviation in the specific gravities of aqueous solutions of these substances is comparatively small. On the other hand, methyl acetate and allyl alcohol, likewise the sum of the other components (bases, etc.) which are present in only very small quantities, exhibit marked differences in these respects. Since the total content of methyl acetate and allyl alcohol is only 5–6 per cent, the influence of these components on the specific gravity of wood-spirit can only be small.

It follows, therefore, that if the alcoholometric estimation of wood-naphtha is carried out by means of the same methods, instruments and tables as are used for ethyl alcohol, the result represents the *sum* of the percentages by weight of methyl alcohol and acetone present, with a sufficient degree of accuracy for practical purposes. Accordingly, the sale of crude wood-spirit on the same basis as ethyl alcohol would appear to be justified, at any rate as far as the honest vendor is concerned.

For the purchaser, however, the position is entirely different. As a refiner, the most important matter for him is not a percentage by weight made up by a number of different components, but the actual amounts of methyl alcohol and acetone present in the product. The purchaser must therefore be in a position to carry out a precise examination of the product whenever he considers it necessary. Partly from the results of this examination and partly from his own experience he is then able to judge immediately whether the composition of his raw material is in any way abnormal.

The examination of crude wood-spirit extends to :—

Methyl alcohol,
Acetone,
Allyl alcohol, •
Methyl acetate,
Anilmonia, amines, pyridine, etc. •

2. Estimation of Methyl Alcohol in Crude Wood-Spirit.—
No really reliable method of estimating methyl alcohol in crude wood-spirit exists. The usual method, which consists in converting methyl alcohol into methyl iodide and estimating the latter by measurement, only gives approximate results, since all methoxy- and ethoxy-compounds form volatile iodides under the conditions of the experiment; hence this method

cannot be used for ascertaining whether a sample of highly refined methyl alcohol is free from the last traces of impurity.

On the other hand, the method is quite useful for determining the approximate content of methyl alcohol in a crude product.

This method was first employed by Krell¹; it was elaborated later by Grodzky and Krämer²; and more recently it underwent further modification, which rendered it simpler to manipulate, in the British Government Laboratory. The modified method is described in detail in the British specification for wood-naphtha (p. 432).

It should be noted that the accuracy of the method depends largely on the nature of the apparatus employed. The use of corks, rubber stoppers and rubber connections should be avoided as far as possible; it is also an advantage if the condenser can be changed from the vertical to the inclined position without disconnecting the flask. If the method is to be used frequently, it will be advisable to have a special apparatus constructed by a glass blower. In order to reduce the sources of error, both the flask and condenser tube should be very small in diameter.

Another method, likewise based on the conversion of methyl alcohol into methyl iodide, is that of Zeisel. Stritar's modification³ of this method has already been described in connection with the estimation of methyl alcohol in crude pyroligneous acid (p. 390). Zeisel's method is more exact than Krell's method, since it depends, not on a somewhat uncertain measurement of methyl iodide, but on the conversion of methyl iodide into silver iodide which can be accurately weighed.

Information regarding the effect of the presence of methyl acetate on the estimation of methyl alcohol as methyl iodide will be found in the British specification for wood-naphtha (p. 432).

As a means of ascertaining whether a portion of the methyl alcohol has already been extracted from the sample of wood-naphtha under examination, the methyl iodide method always proves satisfactory.

It should be noted that the presence of ethyl alcohol cannot be detected by this method of estimation, since the ethyl

¹ Ber., 1873, 6, 1310.

² Ber., 1874, 7, 1492.

³ Zeit. anal. Chem., 1903, 42, 579; 1904, 43, 387.

iodide which it forms is estimated as methyl iodide. If adulteration with ethyl alcohol is suspected, a portion of the wood-spirit should be dehydrated with potassium carbonate and its boiling point determined. The presence of any considerable quantity of ethyl alcohol is easily detected by this test.

An even more delicate test consists in determining the boiling point and specific gravity of the mixture of volatile iodides constituting the distillate in the above method of estimation.

Methyl iodide boils at $42.3^{\circ}\text{C}.$, ethyl iodide at $72^{\circ}\text{C}.$; the specific gravity of methyl iodide is 2.2851 at $15^{\circ}\text{C}.$, but that of ethyl iodide is only 1.943 at $15^{\circ}\text{C}.$

Apart from this method, which will always serve quite satisfactorily, numerous more or less complicated methods for detecting the presence of ethyl alcohol in methyl alcohol are given in the literature.¹

The actual content of methyl alcohol in the crude wood-spirit having been determined by one of the above methods, the estimation of the remaining components is only of secondary interest, and serves chiefly to give an idea as to the probable yields of denaturing wood-spirit and pure methyl alcohol.

3. Estimation of Acetone.—A rough method of estimating acetone in wood-spirit has already been described in connection with the manufacture of pure methyl alcohol (p. 255). This method depends on the insolubility of acetone in sodium hydroxide solution (sp. gr. 1.3), with which, on the contrary, methyl alcohol is miscible. It is carried out by shaking 20 c.c. of wood-naphtha thoroughly with 40 c.c. of the sodium hydroxide solution in a graduated stoppered cylinder, and then allowing the mixture to stand for half-an-hour. At the end of this period a layer of acetone, which is usually coloured dark brown by aldehyde-resin, etc., has separated out at the surface of the mixture, and its volume may be read.

If a more exact estimation of the acetone content is required, two methods are available, namely: (1) *The Gravimetric Method of Krämer*²; (2) *The Volumetric Method of Messinger*.³

¹ Riche and Bardy, *Compt. rend.*, 1876, **82**, 768; *Rupp*, *Chem. Zeit. Rep.*, 1887, p. 25.

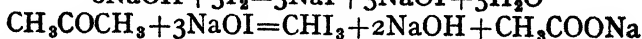
² *Ber.*, 1880, **13**, 1000.

³ *Ber.*, 1888, **21**, 3366.

Both methods depend on the quantitative conversion of acetone into iodoform, which can be effected without difficulty.

Krämer's method was used quite universally at one time for determining acetone in the purer grades of methyl alcohol as well as in denaturing wood-spirit. In the former case it is still applied, but the Excise authorities and the Government powder factories now prefer the method of Messinger, which is more rapid and if properly manipulated gives very uniform results. Precise instructions as to the procedure in carrying out the latter method will be found in the various official specifications for wood-naphtha given below.

Method of Krämer.—This method is based on the fact that in the presence of alkali and excess of iodine, acetone is converted quantitatively into iodoform according to the following equations :—



The iodoform which results from this reaction is dissolved in ether, the volume of the ethereal solution is ascertained, an aliquot portion is evaporated on a weighed clock glass, and the residue is dried and weighed.

The wood-spirit used for analysis must be diluted with water until the acetone concentration is only about 1 per cent. With solutions of higher concentration, using the same quantities of reagents as specified below, the results of the analysis are too low.¹ It is advisable, therefore, to ascertain the approximate content of acetone in the wood-spirit before commencing the analysis, for which purpose the method of shaking with sodium hydroxide described above serves quite well.

The estimation is carried out by introducing 1 c.c. of the sufficiently diluted wood-spirit into an accurately graduated cylinder with a well-ground stopper, or better into a Röse apparatus of suitable size provided with a very closely fitting stopper. 10 c.c. of 2*N*-sodium hydroxide are then added, the mixture is well shaken, and 5 c.c. of 2*N*-iodine solution are run in drop by drop, the contents of the cylinder being shaken gently at the same time.

The iodoform which separates out is then dissolved by shaking the contents of the cylinder with 10 c.c. of ether. The ether

¹ Cf. *Arachequesne*, Compt. rend., 1890, 110, 642; *Vignon*, Compt. rend., 1890, 110, 534; 1891, 112, 873; *Hintz*, Zeit. anal. Chem., 1888, 27, 182.

must be absolutely free from ethyl alcohol, which also produces iodoform, and it must not give any reaction with either potassium hydroxide or potassium iodide. Impure ether, which does conform to the tests with potassium hydroxide and potassium iodide specified in the various Pharmacopœias,¹ usually liberates iodine during the evaporation of the ethereal solution, and thus causes loss. Great care must be taken to avoid losing any of the ethereal solution; it is essential; therefore, that the stopper should fit perfectly.

After the iodoform has been dissolved completely by careful shaking, the apparatus is placed in water at 15° C. and the volume of the ethereal layer is read. An aliquot portion—5 c.c.—is then withdrawn, and allowed to evaporate in diffused daylight on a weighed clock glass in a position where it is unlikely to be contaminated by dust. The residual iodoform is dried in a vacuum desiccator over fresh sulphuric acid and weighed. The weight is usually constant after two hours. One molecule (394) of iodoform is equivalent to one molecule (58) of acetone.

Assuming that 1 c.c. of the diluted wood-naphtha is used for the estimation, the percentage by weight of acetone in the wood-spirit is calculated as follows:—

$$\begin{array}{l}
 \text{If } v = \text{c.c. of wood-naphtha used for pre-paring the dilute solution} \\
 s = \text{specific gravity of the wood-naphtha} \\
 V = \text{total volume in c.c. of the dilute solution} \\
 n = \text{total volume in c.c. of the ethereal iodoform solution at } 15^{\circ} \text{ C.} \\
 m = \text{the aliquot portion in c.c. of the ethereal solution evaporated} \\
 a = \text{the weight of iodoform obtained} \\
 \text{then} \\
 V \frac{a \times 0.1472 \times n}{m \times s} \times 100 = \text{grams acetone in 100 grams of wood-naphtha.}
 \end{array}$$

Chiefly owing to the fact that Krämer's method requires at least 2–3 hours to carry out, the volumetric method of Messinger, which only requires about twenty minutes, is

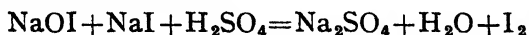
¹ Cf. "Æther purificatus," British Pharmacopœia, 1914, p. 33.

generally preferred. Krämer's method always gives lower results than Messinger's method, the difference being particularly marked when the proportion of acetone in the product undergoing analysis is very small, as for example in "pure" methyl alcohol containing about 0.03 per cent of acetone. In these cases any source of error in the analysis, however small, will influence the result, and it is by no means rare to find that when Krämer's method shows 0.02 per cent of acetone, Messinger's method shows 0.04 per cent for the same product—that is, double the amount. If the proportion of acetone is considerable, this difference remains within normal limits, and from a practical point of view the results obtained by the two methods are identical.

Method of Messinger.—This method is a volumetric modification of Krämer's method. Like the latter it depends on the conversion of acetone into iodoform in the presence of excess of iodine and alkali, according to the equations given on p. 420.

The excess of iodine is present in solution as sodium hypoiodite and iodide.

Accordingly, if the mixture is acidified after the formation of iodoform is complete, the whole of the iodine apart from the amount which has reacted to form iodoform, will be liberated and may be estimated by titration with thiosulphate solution in the usual manner.



The following solutions are required for carrying out the estimation :—

1. *N*-sodium hydroxide.
2. *N*/5-iodine.
3. *N*-sulphuric acid.
4. *N*/10-sodium thiosulphate.
5. Fresh starch solution.

The starch solution should be made up shortly before use by shaking crushed wafers of starch (obtainable at any druggist's) with lukewarm water, and filtering. This operation occupies only a few minutes and results in a perfectly clear solution which gives a sharp indication.

In wood-spirit refineries, etc., where it is necessary to carry out numerous estimations each day, it is advisable to employ burettes which can be filled directly from the stock-bottles

containing the standard solutions, by means of one of the well-known filling arrangements.¹

Before the reagents are utilised, they must be submitted to a blank test for the purpose of ascertaining whether any impurities which may interfere with the analysis are present.²

For this purpose 25 c.c. of *N*-sodium hydroxide are placed in a bottle of 250 c.c. capacity, provided with a well-ground stopper, and 25 c.c. of *N*/5-iodine solution are added. The bottle is allowed to stand for ten minutes at room temperature, 26 c.c. *N*-sulphuric acid are added, and the mixture is titrated with *N*/10-thiosulphate, using starch solution as the indicator.

If the solutions have been standardised exactly, not more than 50 c.c. of *N*/10-thiosulphate should be required. Should there be any variation from this figure, the necessary correction must always be applied when the same solutions are used for the estimation of acetone.

In order to obtain concordant results by this method, it is absolutely necessary to use at least 25 per cent excess of iodine.

If the content of acetone in the product under examination is unknown, a rough estimation must be made by shaking with sodium hydroxide (see p. 255). If no separation of acetone takes place, it is usually safe to conclude that less than 8 per cent is present.

A sample of the product is then diluted with water until the acetone content of the solution is about 0.5 per cent, and the estimation is carried out as follows:—

Ten c.c. of the dilute solution are placed in a stoppered bottle of 250 c.c. capacity, similar to that used for the blank test described above, 50 c.c. of *N*-sodium hydroxide are run in, the mixture is well shaken, and 50 c.c. of *N*/5-iodine solution are then added slowly drop by drop. The mixture is allowed to stand for ten to fifteen minutes, and 52 c.c. of *N*-sulphuric acid are then added. The liberated iodine is titrated with *N*/10-sodium thiosulphate solution, starch solution being added towards the end of the titration. Half the number of c.c. of *N*/10-thiosulphate used are deducted from the number of c.c. of *N*/5-iodine solution used, applying any corrections

¹ cf. "Technical Methods of Chemical Analysis," Lunge and Keane, Vol. I, Pt. I, p. 51.

² Pure sodium hydroxide should be used for the preparation of the standard solution; the ordinary commercial form may contain nitrite, which will affect the result of the analysis.

which the blank test has shown to be necessary. The difference represents the amount of $N/5$ -iodine solution which has reacted with the acetone to form iodoform.

If 10 c.c. of the dilute solution are used, the weight of acetone contained in 100 grams of the original wood-naphtha is calculated as follows :—

If v = c.c. of wood-naphtha used
for preparing the dilute
solution $v \times s$ = grams of wood-
naphtha used
 s = specific gravity of the
wood-naphtha

V = total volume in c.c. of the dilute solution

n = c.c. of $N/5$ -iodine solution required (1 c.c. of
 $N/5$ -iodine = 0.0019353 gram acetone)

then

$$\frac{V \times n \times 0.0019353}{v \times s} = \text{grams acetone in 100 grams of wood-naphtha.}$$

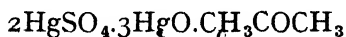
Various modifications of Messinger's method are described below in the subsection dealing with the examination of denaturing wood-naphtha.

Method of Denigès.—A further method of estimating acetone, either gravimetrically or volumetrically, is due to Denigès,¹ and is given here as described by that author.

This method is based on the property exhibited by acetone, in presence of a large excess of mercuric sulphate, of giving a crystalline precipitate possessing the following composition :—



This substance on being dried at 110° C. is converted into the compound :—



The high molecular weight of the former compound renders it possible to detect the presence of very small amounts of acetone. The reagent is prepared by dissolving 5 grams of mercuric oxide in a hot mixture of 20 c.c. of sulphuric acid and 100 c.c. of water; it may be used for the detection or quantitative determination of acetone in water, methyl-alcohol

¹ Journ. Pharm. Chim., 1899 [vi], 9, 7. Bull. Soc. Chim., 1898 (iii), 19, 754; 1899, 21, 241. Compt. rend., 1898, 126, 1868.

See also the modified Denigès' method of Büttner and Wislicenus in the subsection on pyroligneous acid (p. 392).

or ethyl alcohol. Aqueous solutions for testing *qualitatively* by this method must not contain more than 10 grams of acetone in a litre; on the other hand, methyl alcohol solutions may contain as much as 20 grams in a litre. If a larger content of acetone is suspected, the solutions must be diluted accordingly.

Two c.c. of an *aqueous solution* are treated with 2 c.c. of the reagent, and the mixture is heated in a vigorously boiling water-bath for ten minutes. If acetone is absent, the liquid will remain clear; if it is present, the mixture, after being heated for not less than forty-five seconds, will suddenly become turbid or form a precipitate. Even 2 centigrams of acetone in a litre can be detected in this way. In testing *methyl alcohol solutions* 1 c.c. is diluted with 1 c.c. of water (concentrated methyl alcohol precipitates the mercuric sulphate), and 2 c.c. of the reagent are added. The limit of sensitiveness in this case is 3 centigrams in a litre of the original solution. *Ethyl alcohol solutions* must be diluted until the alcohol content is reduced to not more than 2 per cent; the limit of detection is 1 gram in a litre of the original solution.

QUANTITATIVE ESTIMATION.—25 c.c. of the acetone solution, which must not contain more than 0.05 gram of acetone, 10 per cent of methyl alcohol or 1 per cent of ethyl alcohol, are placed in a flask of 90 c.c. capacity, and 25 c.c. of the reagent are added. The mixture is heated in a boiling water-bath for ten minutes, and then allowed to cool. The precipitate is collected on a tared filter, washed with 75–100 c.c. of cold water, dried at 100° C. and weighed. The weight of the precipitate multiplied by 0.06 gives the weight of the acetone present in the 25 c.c. of liquid used for the estimation.

VOLUMETRIC MODIFICATION OF DENIGÈS METHOD.—The estimation can be performed more rapidly by determining the amount of mercury which remains in solution after the precipitate has been removed. The precipitation is carried out exactly as described above. The precipitate is filtered and washed until the filtrate and washings amount to nearly 100 c.c., and the liquid is then made up to exactly 100 c.c.; 20 c.c. of this liquid are mixed with 15 c.c. of ammonia, 50–60 c.c. of water and 10 c.c. of potassium cyanide solution (13 grams in 1 litre). A few drops of 20 per cent potassium iodide solution are added, and the mixture is titrated with

N/10-silver nitrate until a slight permanent turbidity is produced. If *n* be the number of cubic centimetres of *N*/10-silver nitrate solution required, and *x* be the quantity of acetone present in 1 litre of the liquid, of which 25 c.c. were taken for the test, then

$$x = (n - 0.4) \times 0.3 \text{ grams.}^1$$

Since the 25 c.c. of solution used for the analysis must not contain more than 0.05 gram of acetone, it is necessary to make an approximate determination of the acetone content beforehand. For this purpose Denigès uses what may be termed a "chronometric" method, which depends on the fact that the period which elapses before the sudden appearance of the mercury-acetone precipitate is inversely proportional to the acetone content. 2 c.c. of the mercury reagent are mixed with 2 c.c. of the acetone solution, preferably diluted to 1 in 100. The mixture is placed in a glass tube 16–18 cm. in length with an internal diameter of 18 mm., and the tube is shaken and then immersed in a conical flask half-filled with water which is kept boiling vigorously. The number of seconds which elapse from the moment at which the tube is immersed to the sudden appearance of turbidity in the mixture is noted. If this period is less than ninety seconds the liquid must be diluted still further—for example, to one-fifth of its strength if the period is a minute, and to one-half if the period is seventy-five seconds. On the other hand, if the period is much longer than three minutes, the dilution of the original liquid must not be carried so far in the first place. The strength of the solution for analysis should be adjusted so that the acetone content is approximately 2 grams per litre; at this strength the turbidity will appear in about ninety seconds.

4. Estimation of Allyl Alcohol. The third component of interest to the purchaser of wood-naphtha is allyl alcohol ($\text{CH}_2\text{:CH.CH}_2\text{OH}$), of which, however, only a relatively small proportion (0.3–0.5) per cent is present. Since mixtures of allyl alcohol and water boil between 90° and 100° C., the former

¹ "In this formula 0.4 is the volume of silver solution which would be required if there were no acetone present and if the solutions of potassium cyanide and mercuric sulphate were of the exact strength stated. As these solutions will rarely be exact in titre, it is better to carry through a blank experiment with the measured quantities stated, but no acetone, and to substitute the volume of silver nitrate required under these conditions for the 0.4 of Denigès' formula."—Allen's "Commercial Organic Analysis," 4th ed., Vol. I, p. 108.

is found chiefly in the "last runnings" obtained during the rectification of methyl alcohol. Allyl alcohol is isolated from the "last runnings" in the manner already described (p. 259) and is added in certain proportions to denaturing wood-naphtha.

The estimation of allyl alcohol depends on its property, as an unsaturated alcohol belonging to the group $C_nH_{2n}O$, of forming an addition compound with bromine, two atoms of bromine (160 grams) being taken up by every molecule (58 grams) of allyl alcohol.

In addition to allyl alcohol, however, both crude wood-naphtha and denaturing wood-naphtha contain other unsaturated components which are also capable of taking up bromine; consequently, the above method of estimation gives a figure which represents, not merely the content of allyl alcohol, but rather the sum of the unsaturated compounds present. The methods of preparing the bromine solution and of carrying out the estimation are described fully in the German, Austrian and British specifications for denaturing wood-naphtha.

5. Estimation of Methyl Acetate. This compound is formed by the interaction of methyl alcohol and acetic acid, in the form of vapour, during the process of carbonisation.

Crude pyroligneous acid always contains a considerable proportion of methyl acetate, which is partially decomposed into methyl alcohol and acetic acid when the vapour of pyroligneous acid is passed through milk of lime, as in the three-vessel process, or when the liquid acid is neutralised and the neutral liquor is boiled subsequently to drive off the naphtha. A further amount is decomposed during the rectification of the aqueous naphtha, which is usually carried out with addition of lime. A certain quantity, however, escapes saponification; consequently, methyl acetate is always a component of crude wood-spirit.

The estimation of methyl acetate is performed by saponifying with sodium hydroxide, according to the method described in the British specification for wood-naphtha (p. 432).

6. Estimation of Basic Substances. The content of basic substances (ammonia, amines, pyridine, etc.) is given approximately by the "methyl orange alkalinity" of the sample. (See British specification for wood-naphtha, p. 432.)

Examination of Denaturing Wood-Naphtha.

In spite of the fact that numerous different materials have been proposed in the past as denaturants for industrial spirit, and new suggestions come forward each year, no material so nearly approaches a perfect denaturant as crude wood-naphtha.

The value of wood-naphtha as a denaturant, capable of rendering alcohol sufficiently nauseous to prevent its being drunk, depends not so much on the methyl alcohol present as on the other components, namely, aldehydes, ketones, allyl alcohol and organic bases. Up to the present, no satisfactory or at any rate easily available method of separating these substances completely from denatured alcohol has been evolved. Pure methyl alcohol, if mixed with ethyl alcohol, would not render the latter less palatable; there is, however, considerable evidence showing that methyl alcohol is distinctly more poisonous than ethyl alcohol.¹

The specifications and methods of examination authorised by the Governments of various countries for denaturing wood-naphtha are given below:—

(g) German Official Specification for Wood-Naphtha.

1. *Colour*.—The colour of the wood-naphtha shall not be darker than that of a freshly prepared mixture of 2 c.c. *N*/10-iodine with a litre of distilled water. In doubtful cases the comparison is made in glass cylinders 150 mm. long and of about 15 mm. internal diameter, which are closed with circular glass plates held in position by screw-caps having a central circular aperture 12 mm. in diameter. The cylinders are held directly towards the light.

2. *Boiling Range*.—100 c.c. of the wood-naphtha are placed in a short-necked copper flask of about 200 c.c. capacity, resting on an asbestos plate in which is cut a circular hole (diameter about two-thirds that of the flask). The neck of the flask is fitted with a fractionating tube 170 mm. long and of 12 mm. internal diameter, having a bulb 35 mm. in diameter 55 mm. below the upper end of the tube, and a side tube 25 mm. below the upper end of the tube. The fractionating tube is fitted with a short thermometer. The side tube is

¹ Cf. Simmonds, "Alcohol," p. 140.

connected with a condenser provided with an adapter which delivers the distillate into a measuring cylinder graduated in cubic centimetres. The distillation is so conducted that about 5 c.c. of distillate are obtained per minute. At 75° C. at least 90 c.c. should have distilled over.

3. *Miscibility with Water.*—30 c.c. of the wood-naphtha, when shaken with 60 c.c. of water, shall give a clear solution or a solution which is so slightly turbid or opalescent that five to ten minutes after mixing it is still possible to read print in German italics¹ through a column of the liquid 150 mm. high. In doubtful cases the glass cylinders provided for the colour test (1) should be used, holding them directly over the print.

4. *Methyl Alcohol Content.*²—50 c.c. of a mixture composed of 12 parts by weight of acetic anhydride and 88 parts by weight of purified pyridine are placed in a flask of at least 250 c.c. capacity, and 1-1.5 grams of the naphtha, which has been weighed exactly to a milligram in a weighing bottle or weighing tube, are added. The flask is attached to a reflux condenser, the inner tube of which is ground to fit the neck of the flask. The flask is immersed to the neck in vigorously boiling water, allowed to remain for forty minutes, and then cooled. The contents of the flask are mixed with 50 c.c. of water, allowed to remain for ten minutes, and again cooled; a granule of phenolphthalein is then introduced, and *N*-sodium hydroxide solution is added with continual shaking until the red colouration remains permanent for at least a brief period. The main bulk of the sodium hydroxide solution is added from a pipette, the remainder from a burette, as quickly as possible.

A blank test is also carried out as above, in order to determine the volume of *N*-sodium hydroxide solution which is equivalent to 50 c.c. of the mixture of acetic anhydride and pyridine. The difference between the volumes of *N*-sodium hydroxide solution used for the two titrations shall not amount to more than 1 c.c. for every 0.078 gram of wood-naphtha taken. For example, not more than 16 c.c. of *N*-sodium hydroxide shall be required for 1.248 grams of wood-naphtha.

¹ Schwabacher Druckschrift.

² H. Oldekop, *Zeitschrift für Untersuchung der Nahrungs- und Genussmittel*, 1913, 26, 129. German regulations introduced in 1913 stipulated that wood-naphtha for denaturing purposes must not contain more than 40 per cent of methyl alcohol.

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5. *Acetone Content.*

- (a) *Separation on Shaking with Sodium Hydroxide Solution.*—30 c.c. of the wood-naphtha are shaken with 60 c.c. of sodium hydroxide solution of sp. gr. 1.30 (27 grams of sodium hydroxide in 100 grams). After the mixture has been allowed to stand for half an hour, the upper layer shall amount to at least 7.5 c.c.
- (b) *Titration with Iodine Solution.*—10 c.c. of the naphtha are diluted with water to 1 litre. 10 c.c. of the dilute solution are mixed with 20 c.c. of *N*-sodium hydroxide, and 50 c.c. of *N*/10-iodine solution are added with continual shaking. After at least three minutes, the mixture is acidified with 21 c.c. of *N*-sulphuric acid, and the liberated iodine is titrated with *N*/10-sodium thiosulphate solution, starch solution (1 gram of soluble starch in 100 c.c. of water) being added towards the end of the titration. Not more than 28 c.c. of *N*/10-thiosulphate shall be required for the titration.

6. *Allyl Alcohol Content.*—2.447 grams of potassium bromate and 8.719 grams of potassium bromide, which have been tested for purity and dried for at least two hours at 100° C. before weighing, are dissolved in water, and the solution is made up to 1 litre. 20 c.c. of this solution are mixed with 10 c.c. of *N*-sulphuric acid and 5 c.c. of potassium iodide solution (10 grams KI in 100 grams). The liberated iodine is titrated with *N*/10-sodium thiosulphate solution and starch. Not less than 17.3 c.c. and not more than 17.9 c.c. of *N*/10-thiosulphate shall be required.

100 c.c. of the solution of bromine salts are mixed with 20 c.c. of sulphuric acid (38 grams H_2SO_4 in 100 grams). To this mixture the wood-naphtha is added from a burette, in full daylight with continual shaking and finally drop by drop, until the colour of the mixture has been permanently discharged. Not less than 20 c.c. and not more than 30 c.c. of wood-naphtha shall be required.

7. *Methyl Acetate Content.*—10 c.c. of the wood-naphtha are diluted with about 50 c.c. of water and a few drops of phenolphthalein solution (1 gram phenolphthalein in 500 c.c. alcohol). For the purpose of neutralising free acid, *N*/10-sodium hydroxide solution is added to the mixture until the red coloura-

tion is permanent for at least a brief period. 20 c.c. of *N*-sodium hydroxide solution are added, and the mixture is gently boiled under a reflux condenser for a quarter-of-an-hour. The excess of sodium hydroxide is then titrated immediately with *N*-sulphuric acid, of which at least 10 c.c. shall be required.

(h) Austrian Official Specification for Wood-Naphtha.

1. *Colour*.—The naphtha must be colourless or only slightly yellow. In carrying out the test for colour, a sampling bottle is filled with the naphtha and placed alongside the standard colour on white paper, so that the colour of a layer of naphtha 5 cm. thick can be compared with the standard colour. The sampling bottle consists of a colourless glass bottle with parallel walls, the inner surfaces of which are 5 cm. apart.

The *standard colour* consists of a glass plate possessing a definite yellow tint. These plates are supplied by the Experimental Station for Agricultural Chemistry in Vienna.

2. *Distillation*.—100 c.c. of the naphtha are placed in a metal flask of approximately 300 c.c. capacity. The neck of the flask is fitted with a fractionating tube having a bulb and a side tube which is connected with a Liebig condenser. Into the upper end of the fractionating tube, an officially certified thermometer, graduated in hundredths, is inserted in such a manner that its bulb extends below the opening of the side tube. More than one-half of the thermometer scale must be inside the fractionating tube, exposed to the vapour. The flask must be heated in such a manner that the distillate leaves the condenser only in drops. The distillate is received in a graduated glass cylinder, and when the thermometer stands at 80° C. under normal pressure (760 mm.) at least 90 c.c. shall have distilled over. If the pressure is other than normal, then for every 30 mm. over or under 760 mm. the distillation must be stopped at a temperature of 1° C. over or under 80° C.; for example, if the barometer stands at 750 mm. at least 90 c.c. shall have distilled over when the thermometer has reached 79.7° C.

3. *Miscibility with Water*.—A solution prepared by mixing 5 parts by volume of the naphtha with 95 parts by volume of alcohol shall form a clear or only slightly opalescent mixture on addition of double the quantity of distilled water.

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4. *Behaviour towards Salt Solutions.*—When 25 c.c. of the naphtha are shaken with 50 c.c. of a saturated aqueous solution of Chili saltpetre, an oily layer of at least 3 c.c. must separate at the surface of the aqueous liquid. The test is performed in a stoppered flask, the neck of which is graduated in fourths of a cubic centimetre. The capacity of the flask up to the lowest graduation is 50 c.c. and up to the highest graduation 75 c.c. The liquid must be shaken for half-a-minute, not too vigorously and with the flask held horizontally.

5. *Behaviour towards Sodium Hydroxide Solution.*—When 20 c.c. of the naphtha are thoroughly shaken with 40 c.c. of sodium hydroxide solution (sp. gr. 1.30) and the mixture is allowed to stand for half-an-hour, an oily layer of at least 7 c.c. must separate at the surface.

6. *Absorption of Bromine.*—2.447 grams of potassium bromate and 8.719 grams of potassium bromide, which have been dried for two hours at 100° C. before weighing, are dissolved in water, and the solution is made up to 1 litre. 100 c.c. of this solution are placed in a colourless glass bottle of 200 c.c. capacity provided with a well-ground stopper, and 20 c.c. of dilute sulphuric acid (prepared by mixing 3 parts by volume of water with 1 part by volume of conc. sulphuric acid) are added. The stopper is replaced, and the contents of the bottle are cooled to 17.5° C. 10 c.c. of the naphtha are then added from a pipette, the mixture is shaken repeatedly, and the colour observed. Within a period of twelve minutes after addition of the wood-naphtha, the colour must have been completely discharged.

(1) British Official Specification for Wood-Naphtha.

The wood-naphtha must be sufficiently impure to impart to the methylated spirits, prepared by mixing 1 part of the wood-naphtha with 9 parts of spirits of wine, such an amount of nauseousness as will, in the opinion of the Principal of the Government Laboratory, render such mixture incapable of being used as a beverage, or of being mixed with potable spirits of any kind without rendering them unfit for human consumption.

Wood-naphtha submitted for approval should conform to the following tests :—

(a) Not more than 30 c.c. of the naphtha should be required

to decolourise a solution containing 0.5 gram of bromine.

- (b) The naphtha, which must be neutral or only slightly alkaline to litmus, should require at least 5 c.c. of deci-normal acid to neutralise 25 c.c. of the spirit when methyl orange is used as the indicator.

It should contain :—

- (a) Not less than 72 per cent by volume of methyl alcohol.
- (b) Not more than 12 grams per 100 c.c. of acetone, aldehydes and higher ketones, estimated as "acetone" by the formation of iodoform according to Messinger's method.
- (c) Not more than 3 grams per 100 c.c. of esters, estimated as methyl acetate by hydrolysis.

The following details of the manner in which the above tests are conducted in the Government Laboratory are published for the information of the trade :—

Bromine Decolourisation.—A standard bromine solution is made by dissolving 12.406 grams of potassium bromide and 3.481 grams of potassium bromate in a litre of recently boiled distilled water.

Fifty c.c. of this standard solution (=0.5 gram bromine) are placed in a flask of about 200 c.c. capacity, having a well-ground stopper. To this are added 10 c.c. of dilute sulphuric acid (1 in 4) and the whole shaken gently. After standing for a few minutes the wood-naphtha is slowly run from a burette into the clear brown solution of bromine until the latter is completely decolourised. Not more than 30 c.c. of the wood-naphtha should be required for this purpose.

Methyl Orange Alkalinity Test.—The naphtha should be faintly acid to phenolphthalein, slightly alkaline or neutral, rarely acid to litmus, and always alkaline to methyl orange. 25 c.c. of the wood-naphtha are placed in each of two beakers and titrated with deci-normal acid, using in the one case a few drops of litmus solution, and in the other of a solution of methyl orange, as indicator. With litmus, usually 0.1 to 0.2 c.c. of deci-normal acid is required for neutralisation. With methyl

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orange, the total alkalinity should be greater—at least 5 or 6 c.c. of deci-normal acid being required for neutralisation.

The total alkalinity, less that given with litmus, is the "methyl orange alkalinity," and, for the 25 c.c. of wood-spirit, should not be less than is required to neutralise 5 c.c. of deci-normal acid.

Estimation of Methyl Alcohol.—22 grams of coarsely powdered iodine and 5 c.c. of distilled water are placed in a small flask and cooled by immersion in ice-cold water. Then 5 c.c. of the wood-spirit (60.0 o.p.) are added, the flask corked, the contents gently shaken, and allowed to remain in the ice-cold bath for 10–15 minutes.

When well cooled, 2 grams of red phosphorus are added to the mixture of spirit and iodine in the flask, and the latter is immediately attached to a reflux condenser.

The reaction soon commences, and must be moderated by dipping the flask into a cold-water bath. (Spirit may be lost if the reaction is too violent.) After about 15–20 minutes, when all action appears to have ceased, the water bath under the flask is gradually heated to a temperature of about 75° C. (167° F.), and the flask, being occasionally shaken, is allowed to remain at this temperature for 15–20 minutes. The source of heat is then removed and the apparatus left for an hour till it has cooled, when the condenser is reversed, and the methyl iodide slowly distilled off—first at a low temperature—the bath being allowed to boil towards the end of the operation only. The end of the condenser dips into water in a measuring tube, and the iodide is collected under water and measured at a temperature of 15.5° C. (60° F.).

The percentage (by volume) is found from the formula :—

$$\frac{\text{c.c. methyl iodide found} \times 647 \times 100}{\text{c.c. wood-spirit taken}} = \text{Percentage (by volume) of methyl alcohol ;}$$

or, when 5 c.c. of spirit are taken :—

$$\text{c.c. methyl iodide} \times 12.94 = \text{percentage (by volume).}$$

Esters, acetals, etc., also yield methyl iodide by this process, and from the percentage of methyl alcohol calculated as above an amount equivalent to the percentage of these substances present must be deducted. Practically, however, methyl acetate is the only compound usually found in sufficient quantity materially to affect the result. The grams of methyl

acetate per 100 c.c. of spirit multiplied by .5405 give the equivalent of methyl alcohol to be deducted from the total percentage by volume calculated from the methyl iodide found.

The Acetone Reaction.—25 c.c. of normal soda are placed in a flask similar to those used in the bromine reaction. To this is added 0.5 c.c. of the naphtha. The mixture is well shaken, and allowed to stand 5–10 minutes. Into it from a burette *N/5*-iodine solution is run slowly, drop by drop, vigorously shaking all the time till the upper portion of the solution, on standing a minute, becomes quite clear. A few c.c. more of *N/5*-iodine solution are added, as to get concordant results an excess of at least 25 per cent of the iodine required must be added. After shaking, the mixture is allowed to stand for 10–15 minutes, and then 25 c.c. normal sulphuric acid are added. The excess of iodine is liberated, titrated with *N/10*-sodium thiosulphate solution and starch, and half the number of c.c. of thiosulphate solution used are deducted from the total number of c.c. of iodine solution used. The difference gives the amount of acetone by weight in the naphtha by the formula :—

c.c. *N/5*-iodine solution required $\times .3876$ = grams of acetone per 100 c.c. of wood-naphtha.

This includes as acetone any aldehydes, etc., capable of yielding iodoform by this reaction.

If the quantity of "acetone" is excessive, a less quantity of the spirit is taken, or 10 c.c. are diluted with 10 c.c. of methyl alcohol free from acetone, and 0.5 c.c. of the mixture is used.

Estimation of Esters.—5 c.c. of the wood-naphtha are run into a silver pressure flask of about 150 c.c. capacity, together with 20 c.c. of recently boiled distilled water. 10 c.c. of normal soda solution are added, the flask securely closed and digested for at least two hours in a water bath at 100° C. (212° F.). The contents are then washed into a beaker, and titrated with normal acid and phenolphthalein. The difference between the number of c.c. of soda taken and of the acid required for neutralisation may be calculated as methyl acetate (weight in volume) from the formula :—

$$\frac{0.74 \times \text{c.c. soda required} \times 100}{\text{c.c. naphtha taken}} = \text{grams per 100 c.c.}$$

Or if 5 c.c. of spirit are taken as above :—

$$1.48 \times \text{c.c. soda required} = \text{grams of methyl acetate per 100 c.c. of spirit.}^1$$

(k) French Official Specification for Wood-Naphtha.²

The product authorised by the Government for denaturing purposes and known as "Méthylène type Régie" must show a strength of 90° on the alcoholometer, measured at 15° C. without correction. It must contain 25 per cent of acetone, but a variation of 0.5 per cent, more or less, is permitted. It must also contain 2.5 per cent of empyreumatic impurities (after deducting the components saponified by sodium hydroxide and calculated as methyl acetate).

These impurities impart to the alcohol the strong, characteristic odour of the crude products of wood distillation.

The remaining components of the naphtha shall consist only of methyl alcohol and water ; no other substances shall be present.

Any admixture of foreign substances which are not products of the distillation of wood shall be sufficient reason for the rejection of the naphtha.

e. Volumetric Estimation of Acetone in Wood-naphtha.

The following solutions are required :—

1. N/5-iodine solution.—Exactly 127 grams of pure resublimed iodine are weighed out and dissolved in distilled water with addition of 250 grams of potassium iodide ; the solution is then made up to 5 litres at 15° C.

¹ The average composition of wood-naphtha submitted as suitable for denaturing purposes in Great Britain and examined by the foregoing tests may be expressed as follows :—

	Per cent by Volume.
Methyl alcohol	77.3
Ketones, in terms of acetone	10.2
Esters, calculated as methyl acetate	1.3
Unsaturated compounds, calculated as allyl alcohol	0.8
Basic compounds, calculated as pyridine	0.2
Water	(approx.) 12.2

* The exact change in volume occurring when water is mixed with the other ingredients is not known with certainty.—Simmonds, "Alcohol," p. 310.

² Cf. "Alcools," par M. L. Calvet (Paris and Liège, Librairie Polytechnique, C. H. Béranger, Editeur, 1911).

2. *N*/20-thiosulphate solution.—62.025 grams of pure, air-dry sodium thiosulphate are dissolved in distilled water and the solution is made up to 5 litres. 15 c.c. of *N*-sodium hydroxide are then added.

3. Dilute sulphuric acid.—A solution containing approximately 100 grams of sulphuric acid in 1 litre.

4. Sodium hydroxide solution.—A solution containing approximately 80 grams of sodium hydroxide in 1 litre.

Solutions 3 and 4 must be exactly equivalent.

5. Starch paste.—5 grams of starch are stirred with 500 c.c. of distilled water; the mixture is boiled for about an hour and then made up with brine to 1 litre.

Procedure :—

1. Exactly 20 c.c. of the naphtha are measured out and run into a litre flask half-filled with distilled water. The mixture is made up to 1 litre with water, and the liquid is thoroughly shaken until it is homogeneous.

2. 30 c.c. of sodium hydroxide solution are placed in a flask of 250 c.c. capacity.

3. 20 c.c. of the diluted naphtha are added.

4. *N* c.c. of iodine solution (about 55 c.c.) are run in and allowed to act for at least ten minutes, with continual shaking.

5. The liquid is then acidified by adding at least 30 c.c. of dilute sulphuric acid.

6. Thiosulphate solution is added until the liquid is nearly colourless, 4–5 c.c. of starch solution are added, and the titration is continued until the colour is completely discharged.

Before the number of c.c. of iodine solution which have remained in excess can be obtained by subtraction, the number of c.c. (*n*) of thiosulphate solution used must be divided by 4, since the thiosulphate solution has only one-fourth the strength of the iodine solution.

7. From the number of c.c. (*N*) of iodine solution taken, the value $\frac{n}{4}$, which represents the number of c.c. remaining in excess, must be deducted and the resulting figure multiplied by 0.6073.

The formula $(N - \frac{n}{4}) \times 0.6073$ gives the number of parts by volume of acetone contained in 100 parts by volume of the wood-naphtha.

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The analysis must be carried out with the greatest possible accuracy. The value $\frac{n}{4}$ should correspond to at least 10 c.c. of iodine solution.

Example :—

$$N = 49.55 \text{ c.c.}$$

$$n = 41.80 \text{ c.c.}$$

$$\frac{n}{4} = 10.45 \text{ c.c.}$$

$$N - \frac{n}{4} = 49.55 - 10.45 = 39.10$$

$39.10 \times 0.6073 = 23.74$ c.c. of acetone in 100 c.c. of the naphtha.

Note : Should a blank test show that the sodium hydroxide contains salts of nitrous acid, allowance must be made accordingly and the necessary correction introduced into the calculation.

Estimation of "Total Impurities" in Commercial Wood-Naphtha

Apparatus Required.—A Röse tube. This apparatus consists of a vessel, the lower part of which is a cylindrical bulb of 49 c.c. capacity and the upper part a pear-shaped bulb of 200 c.c. capacity. The tube uniting the two parts is graduated from 49 to 55 c.c. in tenths of a cubic centimetre.

Procedure :—

1. Exactly 50 c.c. of pure chloroform, measured at 15° , are introduced into the Röse tube, which must also be kept at 15° C., by means of a pipette fitted with a stopcock and having two graduation marks.

2. A mixture of 25 c.c. of the naphtha, 60 c.c. of water and 38 c.c. of sodium bisulphite solution (sp. gr. 1.35, see *Note A*) is prepared.

After being cooled, the mixture is run into the Röse tube, which is then closed with a well-ground stopper, inverted and shaken thoroughly. When the chloroform has completely separated, its volume is read off on the graduated tube at 15° C. and the increase is noted.

3. By multiplying the increase in the volume of chloroform by 4, the percentage of "total impurities" in the naphtha is obtained.

After determining the total impurities by the above method, the proportion made up of products saponifiable by sodium hydroxide is deducted. The remainder must amount to at least 2.5 per cent.

The *saponifiable products (esters)* are estimated as follows :—

1. 20 c.c. of the naphtha and 50 c.c. of $N/2$ -sodium hydroxide are placed in a flask of 200 c.c. capacity, and a few drops of a 1 per cent alcoholic solution of phenolphthalein added.

2. For the purpose of saponifying the esters the flask is heated on a water-bath for half-an-hour under a reflux condenser.

3. The excess of sodium hydroxide is titrated with $N/2$ -sulphuric acid.

If N = c.c. of sulphuric acid required, then $50 - N$ = c.c. of $N/2$ -sodium hydroxide which have been required for the saponification of the esters.

The quantity of saponifiable products (calculated as methyl acetate) in 100 parts by volume of the naphtha is obtained by means of the formula :—

$$\frac{100 \times (50 - N) \times 0.3894}{n}$$

where n = c.c. of naphtha taken.

If the total impurities exceed 10 per cent, then for every one per cent in excess, the amount of $N/2$ -sodium hydroxide must be increased by 5 c.c.—for example, if 12 per cent of impurities is present, 60 c.c., instead of 50 c.c., must be employed.

The percentage of esters in the naphtha is deducted from the percentage of total impurities as ascertained by the chloroform method.

The *empyreumatic impurities* shall consist exclusively of normal products of wood distillation. The presence of any other substance, whatever its nature, which has been added with the object of falsifying the chloroform test, will lead to the rejection of the naphtha as a denaturant.

Note A.—On adding pure methyl alcohol containing 25 per cent of acetone to solutions of commercial sodium bisulphite and shaking with chloroform, an increase in volume may be obtained, even when the specific gravity of the bisulphite solution is 1.35.

If this be the case, the solution must be standardised in the following manner :—

100 c.c. of the bisulphite solution are introduced into a separating funnel fitted with a stopcock and a glass stopper, and 175 c.c. of water and 50 c.c. of chloroform are added. The mixture is shaken thoroughly, and the two layers are allowed to separate completely. 5 c.c. of the chloroform are run through a filter paper into a test tube, three drops of *N*/5-iodine solution are added, the mixture is well shaken and then observed in order to ascertain if the chloroform has assumed a pink colouration. If the pink colouration disappears, as most usually happens, sodium hydroxide solution (sp. gr. 1.35) is added in small portions, by means of a graduated pipette, to the contents of the separating funnel, and the above test with iodine is repeated after each addition of sodium hydroxide, until the pink colouration of the chloroform remains permanent.

If n = c.c. of sodium hydroxide solution (sp. gr. 1.35) required, then the sodium bisulphite solution will require the addition of $n \times 10$ c.c. of sodium hydroxide solution (sp. gr. 1.35) per litre in order to render it standard.

A test is then made, using the following reagents :—

Methyl alcohol, pure, 90° alcoholometric strength, containing 25 per cent of acetone	25 c.c.
Sodium bisulphite solution, standardised	38 „
Distilled water	60 „
Chloroform	50 „

In these conditions the chloroform layer will show no increase in volume.

(1) United States Official Specification for Methyl Alcohol submitted for Approval as a Denaturing Material.

The methyl alcohol submitted must be partially purified wood-alcohol obtained by the destructive distillation of wood. It must conform to the following analytical requirements :—

Colour.—This shall not be darker than that produced by a freshly prepared solution of 2 c.c. of *N*/10-iodine diluted to 1000 c.c. with distilled water.

Specific Gravity.—It must have a specific gravity of not more than 0.830 at 60° F. (15.56° C.) corresponding to 91° of Tralles' scale.

Boiling Point.—100 c.c. slowly heated in a flask under conditions as described below must give a distillate of not less than 90 c.c. at a temperature not exceeding 75°C . at the normal pressure of the barometer (760 mm.).

100 c.c. of wood-spirit are run into a short-necked copper flask of about 180–200 c.c. capacity, and the flask placed on an asbestos plate having a circular opening of 30 mm. diameter. In the neck of this flask is fitted a fractionating tube 12 mm. wide and 170 mm. long, with a bulb just 1 cm. below the side tube, which is connected with a Liebig's condenser having a water-jacket not less than 400 mm. long. In the upper opening of the fractionating tube is placed a standardised thermometer, so adjusted that its mercury bulb comes in the centre of the bulb. The distillation is conducted in such a manner that 5 c.c. pass over in one minute. The distillate is run into a graduated cylinder, and when the temperature of 75°C . has been reached at the normal barometric pressure of 760 mm., at least 90 c.c. shall have been collected.

Should the barometer vary from 760 mm. during the distillation, 1°C . shall be allowed for every variation of 30 mm. For example, at 770 mm. 90 c.c. should have distilled at 75.3° , and at 750 mm. 90 c.c. should have distilled at 74.7°C .

Miscibility with Water.—It must give a clear or only slightly opalescent solution when mixed with twice its volume of water.

Acetone Content.—It must contain not more than 25 or less than 15 grams per 100 c.c. of acetone and other substances estimated as acetone when tested by the following method (Messinger):—

Determination of Acetone.—1 c.c. of a mixture of 10 c.c. wood-naphtha with 90 c.c. of water is treated with 10 c.c. of double normal soda solution. Then 50 c.c. of *N*/10-iodine solution are added while shaking, and the mixture made acid with dilute sulphuric acid three minutes after the addition of the iodine. The excess of iodine is titrated back with *N*/10-sodium thiosulphate solution, using a few drops of starch solution for an indicator. From 15.15 to 25.8 c.c. of *N*/10-iodine solution should be used by the spirit.

The solution should be kept at a temperature between 15° and 20°C .

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Calculation : X = grams of acetone in 100 c.c. of spirit ;
 Y = number of c.c. of $N/10$ -iodine solution required ;
 N = volume of spirit taken for titration.
 Then, $X = \frac{Y \times 0.096672}{N}$

Esters.—It should contain not more than 5 grams of esters per 100 c.c. of spirit, calculated as methyl acetate and determined as follows :—

Five c.c. of wood-spirit are run into a flask and 10 c.c. normal sodium hydroxide free from carbonates are added, and the flask connected with a return condenser and boiled for two hours. Instead of digesting at boiling temperature the flasks may be allowed to stand overnight at room temperature and then heated on a steam-bath for thirty minutes with an ordinary tube condenser. The liquid after digestion is cooled, and titrated with normal sulphuric acid, using phenolphthalein as an indicator.

Methyl acetate, grams } $= \frac{0.074 \times \text{c.c. of } N\text{-soda required} \times 100}{\text{c.c. spirit taken.}}$
 per 100 c.c. of spirit

Bromine Absorption.—It must contain a sufficient quantity of impurities derived from the wood, so that not more than 25 c.c. or less than 15 c.c. shall be required to decolourise a standard solution containing 0.5 gram of bromine, as follows :—

The standard bromine solution is made by dissolving 12.406 grams of potassium bromide and 3.481 grams of potassium bromate (which is of tested purity and has been dried for two hours at 100° C.) in a litre of water. 50 c.c. of the standard solution containing 0.5 gram of bromine are placed in a glass-stoppered flask having a capacity of about 200 c.c. This is acidified by the addition of 10 c.c. of diluted sulphuric acid (1 to 4) and the whole shaken and allowed to stand a few minutes. The wood-alcohol is then allowed to flow slowly into the mixture, drop by drop, from a burette until the colour is entirely discharged. The temperature of the mixture should be 20° C.

In addition to the above requirements the methyl alcohol must be of such a character as to render the ethyl alcohol with which it is mixed unfit for use as a beverage.¹

¹ In America, chiefly owing to the demand for methyl alcohol for the manufacture of formaldehyde and other industrial purposes, it is no longer compulsory to use wood-naphtha as a denaturant : other materials have now been approved.

(m) Examination of Pure Methyl Alcohol.

As mentioned above, the chief applications for pure methyl alcohol are in the aniline-dye industry, for the manufacture of formaldehyde, and in the preparation of perfumes.

Experience has shown that the yields in the aniline-dye industry are seriously reduced if impure methyl alcohol is employed, and a considerable loss of material results. For example, 1 kilo. of acetone, if present in the methyl alcohol, will react with about 5 kilos. of aniline, rendering it useless for the process.

In consequence, the stipulations of the aniline-dye factories in respect of the purity of methyl alcohol are very strict. The parties interested have agreed on the following specification for the product :—

SPECIFICATION FOR PURE METHYL ALCOHOL

(Maximum acetone content, 0.1 per cent.)

1. Appearance : water-white and absolutely clear.
2. The alcohol must indicate at least 99 per cent on Tralles' alcoholometer at 15° C.
3. It must have a specific gravity of 0.7970 at 15° C.
4. On distillation, at least 98 per cent must pass over within one degree (65.6–66.6° C.) indicated on a thermometer divided into hundredths. Temperature range, 65–70° C.
5. It must be free from foreign components, and the acetone content, estimated by Krämer's method, must not exceed 0.1 per cent by weight.
6. On adding two volumes of concentrated sulphuric acid (66° Bé) to one volume of the alcohol, only a faint yellow colouration, if any, is permissible. A brown colouration must not be produced.
7. When the alcohol is shaken with a concentrated solution of sodium hydroxide in any proportion, no colouration shall be produced.
8. The pink colouration produced on adding 1 c.c. of potassium permanganate solution (1 in 1000) to 5 c.c. of the alcohol must not disappear immediately.
9. A mixture of 25 c.c. of the alcohol and 1 c.c. of bromine solution (1 part of bromine in 80 parts of 50 per cent acetic acid) must retain a yellow colour.

10. The alcohol must be neutral.

11. A few drops of phenolphthalein on addition to the alcohol must not produce a red colouration : on subsequent addition of 1 c.c. of *N*/10-sodium hydroxide solution a distinct red colouration must be produced.

12. The methyl alcohol must be miscible with water in any proportion. No turbidity or precipitate shall appear in the solution, either immediately or after allowing to stand for some time.

As a test of purity the above examination is undoubtedly very thorough.

In performing certain of these tests special precautions must be taken. The *boiling-point determination* (clause 4) must be carried out with the greatest care and with all the precautions which are observed in making a scientific determination, such as complete immersion of the thermometer in the vapour, correction of the barometer reading, etc. ; otherwise, concordant and accurate results cannot be expected. It is essential also that the vendor and the purchaser, both of whom will make an examination of the alcohol, shall agree absolutely as to the details of the apparatus to be employed for determining the boiling point, since the use of different materials—for example, copper instead of glass flasks—may give rise to differences in the results.

The method of determining the boiling point described in the United States specification for wood-naphtha (p. 441) may be adopted ; but in this case it will be advisable to use a water bath for heating the flask, and also a Zincke thermometer, which will allow practically the whole of the scale to be immersed in the vapour.

The corrections given in the specification for variations of the barometer are also applicable to the boiling point of methyl alcohol.

In regard to the *acetone content* (clause 5), it should be noted that consumers usually demand an even higher degree of purity, and in order to meet competition the manufacturers are often compelled to supply a product containing not more than 0.03 per cent of acetone, and possibly even less. For the manufacture of formaldehyde (p. 370) a product containing up to 0.5 per cent of acetone is satisfactory, but it must be free from other impurities, especially traces of inorganic substances such as chlorine and sulphur.

The estimation of acetone by Krämer's method is described in detail on page 420.

In carrying out the *sulphuric acid test* (clause 6), the test glass must be perfectly clean, otherwise a brown colouration may be produced, which will render the test deceptive. It is advisable, therefore, to rinse out the glass once or twice with concentrated sulphuric acid before performing the test.

The *permanganate test* (clause 8) also requires care and great cleanliness. In making up the average sample of methyl alcohol from the glass vessels in which the product is usually shipped, the liquid should not be sucked into the pipette, since in this way it may easily become contaminated with saliva, which in certain circumstances may affect the test.

The best method of taking the sample is to reverse the pipette, dip the wide end into the liquid, close the pointed end with the finger, remove the pipette from the liquid, and allow the contents to flow into the collecting bottle in which the average sample is made up.

In actual fact, the permanganate solution is never decolourised immediately. If the methyl alcohol undergoing the test is impure, the colour will *fade*. Without experience it is not always easy to detect this fading, in which case it is advisable to prepare a standard for comparison, from a sample of methyl alcohol which conforms to the test.

(n) Analytical Control in the Manufacture of Formaldehyde.

1. Examination of Methyl Alcohol.—Methyl alcohol intended for the manufacture of formaldehyde must undergo a very careful examination, especially in regard to acetone content, boiling point, residue on evaporation, and also the presence of esters, since the latter are capable of causing rapid deterioration of the catalyst.

Moreover, the methyl alcohol must be absolutely free from inorganic matter, for example, arsenic, sulphur and chlorine, since these impurities, even in minute quantities, promote the formation of methylal and thus cause loss.

It is only necessary to test for the presence of these substances if any unaccountable diminution in the yield is observed.

Methyl alcohol may contain organic compounds of sulphur,

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arsenic and even chlorine, if the crude wood-spirit from which it is derived has been treated with impure sulphuric acid, hydrochloric acid, calcium chloride, etc. In normal conditions, however, such impurities are absent.

Methyl alcohol is tested for these impurities by burning a portion in a spirit lamp and absorbing the products of combustion in a solution of potassium carbonate to which bromine water has been added, or in a solution of silver nitrate.

2. Examination of Formaldehyde.—This includes :

(a) *Estimation of the Free Acid* by titration with $N/10$ -sodium hydroxide, using phenolphthalein as indicator and calculating as formic acid.

(b) *Estimation of the Formaldehyde ($H.CHO$)*. For this purpose a very large number of methods have been suggested, of which, however, only the following have actually been adopted :—

1. The ammonia method of Legler.¹
2. The iodine method of Romijn.²
3. The hydrogen peroxide method of Blank and Finkenbeiner.³

The iodine method is undoubtedly the most rapid to carry out and gives the sharpest end-point.

*In the ammonia method the end-point can only be recognised by an experienced eye ; in the hydrogen peroxide method the end-point is decidedly sharper, but not absolutely satisfactory.

Unfortunately, the iodine method only gives correct results if substances which produce iodoform (ketones, acetaldehyde, etc.) are absent.

As a general rule the formaldehyde factories use the hydrogen peroxide method.

As mentioned previously, commercial formaldehyde or "formalin" is required to have a strength of 40 per cent "by volume," meaning in this case a solution of which 100 litres contain 40 kilos. of formaldehyde.

It follows, therefore, that if the formaldehyde under examination is *weighed* for analysis instead of being measured, the results must be converted accordingly.

As a rule, however, the manufacturers, in adjusting the strength of the solution to 40 per cent "by volume," do not

¹ Ber., 1883, 16, 1333. ² Zeit. anal. Chem., 1897, 36, 18. ³ Ber., 1898, 31, 2979.

adhere strictly to any particular specific gravity, but furnish a product containing 36.5 per cent by weight of formaldehyde.

Estimation of Formaldehyde by the Hydrogen Peroxide Method.

—This method consists in oxidising the formaldehyde to formic acid in alkaline solution and titrating the excess of alkali. 25 c.c. of 2*N*-sodium hydroxide are placed in a conical flask of 200 c.c. capacity, fitted with a well-ground stopper; the flask and its contents are counterpoised on an analytical balance, and an amount of the formaldehyde solution corresponding approximately to 1 gram of absolute formaldehyde (3 grams of 40 per cent formalin; 1 gram of solid paraform) is weighed into the flask. 50 c.c. of pure hydrogen peroxide (3 per cent by weight) are then added slowly (in about 3 minutes) through a small funnel to prevent splashing.

After standing for a quarter-of-an-hour, the funnel and the walls of the flask are rinsed with water, the flask is allowed to stand, again for a quarter-of-an-hour, and the excess of sodium hydroxide is titrated with *N*- or 2*N*-sulphuric acid, using litmus as indicator.

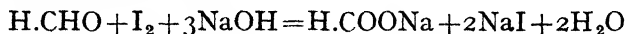
The acid value of 25 c.c. of 2*N*-sodium hydroxide solution in the presence of 50 c.c. of the hydrogen peroxide must be ascertained previously by performing a blank test, using *N*- or 2*N*-sulphuric acid for titration and calculating in terms of 2*N*-sodium hydroxide. From this value the number of c.c. of 2*N*-sodium hydroxide remaining in excess, as determined by the above titration, is then deducted, and the difference represents the number of c.c. used. 1 c.c. of 2*N*-sodium hydroxide is equivalent to 0.06 gram of formaldehyde.

Estimation by the Iodine Method of Romijn.—This method is characterised by its accuracy and simplicity, but it can only be used in the absence of ketones and higher aldehydes. In carrying out the estimation, the presence of these impurities is betrayed by a yellow turbidity, due to the formation of iodoform.

The solution of formaldehyde is diluted to about 2 per cent. 5 c.c. of the dilute solution and 30 c.c. of *N*-sodium hydroxide are introduced into a stoppered bottle of about 500 c.c. capacity, and 40–70 c.c. of *N*/5-iodine solution are added with continual shaking until the liquid is bright yellow. The stopper is replaced, the bottle well shaken and allowed to stand for fifteen minutes. The contents are then acidified

with a slight excess of *N*-hydrochloric acid, and the excess of iodine is titrated with *N*/10-sodium thiosulphate.

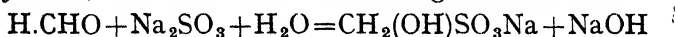
One c.c. of *N*/5-iodine solution is equivalent to 0.003 gram of formaldehyde.



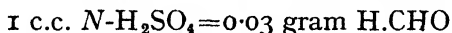
Orloff used the following modification of Romijn's method for his analyses. In the first place the specific gravity of the formaldehyde solution at 15° C. is determined. 5 c.c. of the solution are diluted to 500 c.c. Assuming that the specific gravity of the original solution is 1.077, 5 c.c. = 5.385 grams.

Five c.c. of the diluted solution are treated with 50 c.c. of *N*/10-sodium hydroxide and 30 c.c. of *N*/10-iodine solution. The mixture, after having stood for fifteen minutes, is acidified with 50 c.c. of *N*/10-hydrochloric acid, and the liberated iodine is titrated with *N*/10-thiosulphate.

*Lemme's Method of Estimating Formaldehyde.*¹—This method is said to give satisfactory results, and may be described briefly here; it is based on the following reaction:—

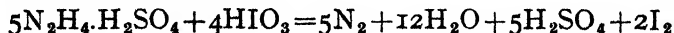


and is carried out by weighing 25–26 c.c. of the formaldehyde solution into a 100 c.c. graduated flask and adding water up to the mark. 10 c.c. of this solution are mixed with 50 c.c. of a 25 per cent solution of sodium bisulphite, which has been neutralised previously with *N*-sodium hydroxide, using two drops of rosolic acid as indicator. The free alkali in the solution is then titrated with *N*-sulphuric acid.



When exact analytical results are required, the acidity of formaldehyde, which may usually be overlooked, must of course be taken into account.

*Riegler's Gas Volumetric Method*² of estimating formaldehyde is based on the following principles: When a solution of iodic acid is mixed with a solution of hydrazine sulphate the whole of the nitrogen is liberated:—



¹ Chem. Zeit., 1903, 27, 896.

² Zeit. anal. Chem., 1901, 40, 92; Journ. Chem. Soc., 1901, 80, ii, 360. See also: "Technical Methods of Chemical Analysis," Lunge and Keane, Vol. II, Pt. II, p. 906.

If formaldehyde is present in the solution, however, it combines with an equivalent amount of hydrazine to form a hydrazone, which is only very slowly decomposed by iodic acid. It is obvious therefore that if a standard hydrazine solution is used, the amount of formaldehyde which has been added can be calculated from the deficiency in the volume of nitrogen liberated by iodic acid.

A solution containing 5 grams of pure iodic acid in 50 c.c. of water, and a solution containing 1 gram of hydrazine sulphate in 100 c.c. of water are required.

Riegler used the well-known Knop-Wagner nitrometer for the estimation. 20 c.c. of the hydrazine sulphate solution are introduced by means of a pipette into the outer compartment of the reaction vessel, and 20 c.c. of water are added. 5 c.c. of the iodic acid solution are placed in the inner compartment. The reaction vessel is then closed with a rubber stopper and immersed in cold water, contained in a tall cylinder, until the stopper is just covered with water. After ten minutes, the level of the water in the graduated tube is adjusted exactly to zero, and the glass tap firmly inserted and turned so as to bring the reaction vessel into communication with the graduated tube. In order to prevent an undue rise of pressure when the reaction starts, 20 c.c. of water are allowed to run out of the graduated tube by opening the pinch cock. The reaction vessel is then removed from the cylinder, shaken vigorously for half-a-minute, and replaced in the cylinder. After two minutes the water-levels in the two limbs of the burette are brought to the same height, and the volume of nitrogen is read. The temperature and pressure are noted, and the volume of gas at 0°C . and 760 mm. is calculated.

Twenty c.c. of the hydrazine solution are then measured accurately into a flask, and a known volume of the formaldehyde solution under examination (the volume taken should not contain more than 0.08 gram of absolute formaldehyde) is added by means of a pipette. The mixture is shaken, allowed to stand for at least fifteen minutes, and then transferred to the outer compartment of the reaction vessel. The flask is washed out with distilled water, and sufficient of the washings to make up, together with the volume of formaldehyde solution taken, about 20 c.c., is added to the contents of the reaction vessel. 5 c.c. of the 10 per cent iodic acid solution are placed in the inner vessel. After ten minutes, the level in the

graduated tube is adjusted to zero, 20 c.c. of water are run out as before, the reaction vessel is shaken for half-a-minute (*not longer*), and replaced in the cooling-cylinder. After two minutes (*not longer*), the water-levels are adjusted and the volume of nitrogen is read off and reduced to 0° C. and 760 mm.

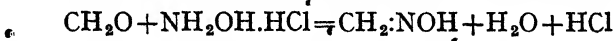
From the difference between the two volumes of nitrogen the formaldehyde content of the solution under examination can easily be calculated. Since *one* molecule of hydrazine combines with *two* molecules of formaldehyde, 1 c.c. of nitrogen at 0° and 760 mm. represents 0.0027 gram of formaldehyde.

Riegler recommends that the volume of nitrogen be read off quickly, since he observed that the iodic acid gradually decomposes the hydrazone with liberation of nitrogen.

A useful criticism of the various methods of estimating formaldehyde has been given by Smith.¹ Williams² has also studied the methods, and his conclusions, generally, agree with those of Smith.

Lockemann and Croner³ have examined several of the better-known methods and conclude that none of those which depend on the separation of formaldehyde and methyl alcohol by distillation is capable of giving exact results. Accordingly, they recommend certain methods whereby the two components are estimated *in presence of one another in solution*. These methods are suitable for the estimation of formaldehyde and methyl alcohol in "formalin" and "paraform"; the results are sufficiently accurate, and the complete analysis can be performed in three-quarters-of-an-hour.

For the estimation of the formaldehyde Lockemann and Croner recommend the method of Brochet⁴ and Cambier,⁴ which consists in adding a solution of hydroxylamine hydrochloride to the formalin solution, diluted to ten times its bulk.



The liberated hydrochloric acid is titrated with *N*-sodium hydroxide solution, using methyl orange as indicator.

One c.c. of *N*-sodium hydroxide corresponds to 0.030 gram of formaldehyde.

¹ Journ. Amer. Chem. Soc., 1903, **52**, 1028.

² Journ. Amer. Chem. Soc., 1905, **27**, 596.

³ Zeit. anal. Chem., 1915, **54**, 11.

⁴ Compt. rend., 1895, **120**, 449.

Lemme's method (see p. 448) is equally suitable.

Lockemann and Croner's method for the estimation of methyl alcohol in formalin is described on page 454.

3. Specific Gravity of Commercial Formaldehyde.—The specific gravity of the commercial product depends not only on its content of absolute formaldehyde, as estimated by one of the above methods, but also on the amount of methyl alcohol which is allowed to remain with the formaldehyde in order to prevent polymerisation, and which can be estimated by one of the methods described below.

The methyl alcohol content must be larger in winter than in summer, but the actual amount left in the product varies in different factories. It follows, therefore, that the specific gravity of commercial formaldehyde cannot be regarded as a standard. As a matter of fact the trade never requires an article of definite specific gravity, except in the case of formaldehyde which is intended for pharmaceutical purposes and must therefore comply with one or other of the pharmacopœia specifications (see below).

Lüttke¹ has drawn up a table of specific gravities of formaldehyde solutions, but this table does not indicate the methyl alcohol content of the respective solutions; consequently it has very little practical value.

SPECIFIC GRAVITIES OF AQUEOUS FORMALDEHYDE SOLUTIONS
AT 18.5° C. (LÜTTKE)²

H.CHO Per cent by weight	Specific gravity.	H.CHO Per cent by weight	Specific gravity.	H.CHO Per cent by weight	Specific gravity.	H.CHO Per cent by weight	Specific gravity.	H.CHO Per cent by weight	Specific gravity.
1	1.002	9	1.023	17	1.041	25	1.064	33	1.078
2	1.004	10	1.025	18	1.043	26	1.067	34	1.079
3	1.007	11	1.027	19	1.045	27	1.069	35	1.081
4	1.008	12	1.029	20	1.049	28	1.071	36	1.082
5	1.015	13	1.031	21	1.052	29	1.073	37	1.083
6	1.017	14	1.033	22	1.055	30	1.075	38	1.085
7	1.019	15	1.036	23	1.058	31	1.076	39	1.086
8	1.020	16	1.039	24	1.061	32	1.077	40	1.087

¹ Pharm. Zeit., 1893, 38, 281.

² These figures refer apparently to solutions of formaldehyde which are comparatively rich in methyl alcohol.

4. Estimation of the Methyl Alcohol Content of Formalin.—This estimation is carried out from time to time in order to ensure that the composition of the formalin is suited to the particular season of the year and, therefore, that any risk of the product becoming turbid owing to the formation of paraformaldehyde is removed. An unnecessarily large content of methyl alcohol represents a heavy manufacturing loss, but this can easily be avoided by exercising suitable analytical control.

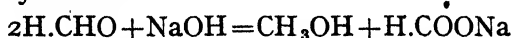
The formaldehyde content is more or less the same for all brands of formalin, but the methyl alcohol content varies from 8 to 18 per cent according to the origin of the product and the season of the year. The specific gravity varies, of course, with the methyl alcohol content.

If, for any given formaldehyde content and specific gravity, the methyl alcohol content is ascertained, it is possible gradually to accumulate sufficient data from which to compile a table showing the relationship between these different values.

Henceforward, in examining formaldehyde solutions, it is only necessary to determine the formaldehyde content and the specific gravity; reference to the table will then give the corresponding methyl alcohol content.

In examining strange brands, which possibly do not fall within the scope of the tables, it is necessary to determine the methyl alcohol content by one of the following methods:—

1. *The Method of the "Verein für chemische Industrie," Mainz,*¹ depends on the conversion of formaldehyde into methyl alcohol and formic acid when it is boiled with a solution of sodium hydroxide:—



100 grams of the formaldehyde solution, of which the formaldehyde content is known, are weighed into a strong, not too small, round-bottomed flask, 700 grams of 2*N*-sodium hydroxide solution are added, and the mixture is boiled for two hours under an efficient reflux condenser above which is a spiral condenser cooled by ice. (The condensers must be sufficiently large and well cooled, otherwise methyl alcohol will be lost.) The apparatus is then allowed to cool, and the flask is removed and connected with an ordinary condenser which must be well cooled. 300–400 c.c. of the

¹ Zeit. anal. Chem., 1900, 39, 62.

liquid are distilled over, and the amount of methyl alcohol in the distillate is ascertained by an accurate determination of the specific gravity. The distillate contains not only the methyl alcohol which was present in the formaldehyde solution, but also that formed as shown by the above equation. Since the formaldehyde content is known, the latter amount can be calculated, and by deducting it from the total methyl alcohol in the distillate, the amount present in the solution used for analysis is obtained; from this figure the percentage content is, of course, easily calculated. The specific gravity of the distillate must be exact to the fourth decimal place, and the sodium hydroxide used must be as pure as possible. The results are always rather low, owing to the fact that a portion of the formaldehyde, in presence of sodium hydroxide, is converted into sugars, etc. The error amounts to about 10 per cent; for example, instead of finding 10 per cent of methyl alcohol, only 9 per cent is found.

2. *The Sulphanilic Acid Method of Gnehm and Kaufler.*¹—This method depends on the condensation of formaldehyde with sodium sulphanilate to form a non-volatile compound, removal of the methyl alcohol by distillation, and determination of the specific gravity of the distillate. 40 c.c. of water are heated to boiling in a small flask, 110 grams of crystallised sodium sulphanilate are added in small portions, and the heating is continued until the salt is completely dissolved. The solution is then cooled rapidly, the crystalline paste which separates out is broken up to some extent with a glass rod, and exactly 20 c.c. of the formaldehyde solution are added. The flask is closed with a cork and allowed to stand for 3–4 hours at room temperature with occasional shaking; or else, it is immersed in a water bath kept at 35–40° C. for 1½–2 hours, in which time the reaction is complete. The flask is then placed in an oil bath, and 30–35 c.c. are distilled off at 125–145° C. The distillate is made up to 50 c.c. and the specific gravity of this solution is determined at 15° C., as accurately as possible, by means of a pycnometer.

3. In the author's opinion the best and most rapid method of estimating the methyl alcohol in formaldehyde solutions is the *bisulphite method* (introduced by the Trebertrocknungsgesellschaft, Cassel).

¹ Zeit. angew. Chem., 1904, 17, 673.

In applying this method Bamberger¹ recommends the following procedure: 50 c.c. of the formaldehyde solution are mixed with 140 c.c. of bisulphite solution containing 1 gram-molecule of sodium hydrogen sulphite in 200 c.c. The mixture is allowed to stand in a well-corked flask for 4-5 hours, until condensation with formation of oxymethylene-sulphonic acid is complete. The mixture is then neutralised exactly with sodium hydroxide. The end-point is determined by "spotting" on paper which has been impregnated with Brilliant Yellow or phenolphthalein, direct addition of phenolphthalein to the solution being inadmissible. (If too much alkali has been added accidentally, the solution is treated with bisulphite solution or dilute sulphuric acid until it exhibits only a faint alkaline reaction.) The flask is then connected to a condenser and heated in an oil bath, until 75 c.c. of liquid have distilled over into a 100 c.c. graduated flask used as the receiver. The flask is filled up to the mark, and the specific gravity at 15° C. is determined by means of a Mohr balance.

The most suitable tables for ascertaining the strength of aqueous solutions of methyl alcohol are those of Doroschewski and Roshdestwenski² (see pp. 455, 415).

4. Lockemann and Croner³ (see p. 451) recommend the following method of determining methyl alcohol in commercial solutions of formaldehyde. The 40 per cent formalin solution is diluted to 100 times its volume with water. 5 c.c. of the dilute solution are mixed in a conical flask of 200 c.c. capacity with 70 c.c. of water and 25 c.c. of alkaline *N*/2-permanganate (15.82 grams KMnO_4 and 40 grams NaOH per litre). The mixture is heated on a steam bath for 15-20 minutes with frequent shaking, and then treated with 20 c.c. of *N*/2-oxalic acid (31.51 grams of crystallised oxalic acid and 75 c.c. of conc. sulphuric acid per litre) which decolourises the solution. The excess of oxalic acid is determined by titration with acid *N*/2-permanganate (15.82 grams of KMnO_4 and 40 grams of crystallised phosphoric acid per litre). From these data the amount of alkaline permanganate used up can be calculated.

¹ Zeit. angew. Chem., 1904, **17**, 1246.

² Journ. Russ. Phys. Chem. Soc., 1909, **41**, 977; Journ. Soc. Chem. Ind., 1910, **29**, 173.

³ Zeit. anal. Chem., 1915, **54**, 11.

The alkaline $N/2$ -permanganate oxidises both the formaldehyde and the methyl alcohol.

One c.c. of the permanganate is equivalent to :—

0.00375 gram of formaldehyde,

0.00267 gram of methyl alcohol.

SPECIFIC GRAVITIES AT $15^{\circ}/15^{\circ}$ C. OF MIXTURES OF PURE METHYL ALCOHOL AND WATER (DOROSCHEWSKI AND ROSHDESTWENSKI)

Methyl alcohol. Per cent by weight.	Specific gravity at $15^{\circ}/15^{\circ}$ C.	Methyl alcohol. Per cent by weight.	Specific gravity at $15^{\circ}/15^{\circ}$ C.	Methyl alcohol. Per cent by weight.	Specific gravity at $15^{\circ}/15^{\circ}$ C.	Methyl alcohol. Per cent by weight.	Specific gravity at $15^{\circ}/15^{\circ}$ C.
0	1.00000	26	0.96047	52	0.91531	78	0.85626
1	0.99814	27	0.95901	53	0.91328	79	0.85374
2	0.99630	28	0.95752	54	0.91124	80	0.85122
3	0.99457	29	0.95601	55	0.90918	81	0.84868
4	0.99285	30	0.95449	56	0.90710	82	0.84610
5	0.99116	31	0.95296	57	0.90500	83	0.84348
6	0.98950	32	0.95139	58	0.90289	84	0.84082
7	0.98787	33	0.94979	59	0.90075	85	0.83815
8	0.98633	34	0.94817	60	0.89859	86	0.83548
9	0.98480	35	0.94653	61	0.89641	87	0.83280
10	0.98327	36	0.94487	62	0.89419	88	0.83010
11	0.98179	37	0.94319	63	0.89195	89	0.82740
12	0.98031	38	0.94149	64	0.88968	90	0.82468
13	0.97887	39	0.93976	65	0.88739	91	0.82196
14	0.97745	40	0.93802	66	0.88510	92	0.81921
15	0.97603	41	0.93625	67	0.88280	93	0.81639
16	0.97462	42	0.93447	68	0.88048	94	0.81356
17	0.97322	43	0.93266	69	0.87816	95	0.81070
18	0.97181	44	0.93082	70	0.87584	96	0.80784
19	0.97040	45	0.92896	71	0.87347	97	0.80498
20	0.96899	46	0.92708	72	0.87109	98	0.80213
21	0.96758	47	0.92517	73	0.86868	99	0.79929
22	0.96617	48	0.92323	74	0.86622	100	0.79647
23	0.96476	49	0.92128	75	0.86376		
24	0.96335	50	0.91932	76	0.86126		
25	0.96192	51	0.91733	77	0.85876		

The formaldehyde content has already been determined (see p. 450), therefore the equivalent amount of permanganate can be calculated. On deducting this amount from the total quantity of permanganate used up, the difference represents

the amount which has been required to oxidise the methyl alcohol, and the content of the latter can easily be calculated.

5. Determination of Free Acid in Commercial Formaldehyde.—Formaldehyde always contains traces of free acid; this is estimated by titration with *N*/10- or *N*/100-sodium hydroxide, and calculated as formic acid.

6. Pharmaceutical Preparations.—For medicinal purposes, a formaldehyde solution possessing a particularly high degree of purity is specified in the pharmacopœias of various countries. The *specification of the British Pharmacopœia* is given below; it includes certain tests which are also suitable for application to the commercial brands of formaldehyde, in cases where any suspicious factors (excessive residue on evaporation, high ash content, etc.) render a more detailed investigation necessary.

Liquor Formaldehydi.¹

SOLUTION OF FORMALDEHYDE.

Solution of Formaldehyde is an aqueous solution containing in 100 millilitres not less than 36 and not more than 38 grams of formaldehyde, CH_2O . Formaldehyde may be obtained by the limited oxidation of methyl alcohol.

***Characters and Tests.**—A colourless liquid with a characteristic, pungent odour. Neutral or slightly acid to *litmus*. Miscible with *water* and with *alcohol* in all proportions. Caustic when applied to the skin. Specific gravity 1.079 to 1.081. Yields, when evaporated to dryness, a whitish, amorphous residue which leaves no appreciable ash on incineration. Yields with solution of *silver ammonio-nitrate* a precipitate of metallic silver. On the addition of 2 drops of the Solution to 5 millilitres of *sulphuric acid*, in which a little *salicylic acid* has been previously dissolved, a deep red colouration is produced. When 1 millilitre is mixed with 10 millilitres of *N*/10 solution of *iodine*, the mixture nearly decolourised with solution of *sodium hydroxide* and warmed, no yellow, crystalline precipitate is produced (absence of acetone). Diluted with four times its volume of *water* it yields no characteristic reactions for iron, copper, lead, calcium, chlorides, or sulphates. Contains in 100 millilitres not less than 36 and not more than 38 grams

¹ "The British Pharmacopœia," 1914 (London, Constable and Co., Ltd.).

of formaldehyde, CH_2O , as determined by the following process :—

To 50 millilitres of *N/1 solution of sodium hydroxide* add 3 millilitres of *Solution of Formaldehyde* and 50 millilitres of *solution of hydrogen peroxide* and warm on a water bath; similarly mix 50 millilitres of *N/1 solution of sodium hydroxide* with 50 millilitres of *solution of hydrogen peroxide* and warm on a water bath. When the reactions are complete and all effervescence has ceased, add a few drops of *solution of phenolphthalein* to each mixture and titrate with *N/1 solution of sulphuric acid*. The difference between the two titrations is not less than 36 and not more than 38 millilitres.

(o) The Analysis of Tar, Tar-Oils and Pine-Oil.

1. Hardwood-Tar.—The examination of hardwood-tar is only rarely carried out in the laboratory of a wood-distillation factory.

As mentioned in Chapter VII, the tar is obtained either by settling the crude pyroligneous acid or by one or other of the processes of extraction already described. The product is treated merely for removal of acid, and is then utilised as fuel or sold. Occasionally, the tar is distilled in fire-heated stills for the purpose of obtaining the heavy oils, and these are sold subsequently to creosote manufacturers.

Only very few wood-distillation factories undertake the manufacture of creosote and for this purpose purchase tar from other factories; consequently, the examination of the tar is limited almost entirely to a determination of the acetic acid content before the product is used as fuel.

The estimation of acetic acid in hardwood- or softwood-tar is carried out most simply by placing 100 grams of the tar in a round-bottomed flask of about 300 c.c. capacity, which is immersed in an oil bath. The flask is provided with a cork bored with three holes, one of which contains a bent glass delivery tube connecting the flask with a Liebig condenser; another contains a glass tube, one end of which is drawn out to a fine point and reaches nearly to the bottom of the flask, the other end being connected with a suitable steam generator. The third hole contains a thermometer, the bulb of which is close to the bottom of the flask and is therefore always covered by the tar.

The oil bath and the steam generator are now heated up.

In the first place, the distillation is carried as far as possible without admitting steam, the oil bath being heated gradually to 130–140° C. As soon as the distillation slackens, the steam generator is connected up and steam is passed in, care being taken that the temperature—measured in the tar—does not exceed 140° C. The process is continued until the distillate contains less than 1 per cent of volatile acids, calculated as acetic acid, the strength being determined by titrating small portions of the distillate from time to time with *N*- or *N*/10-sodium hydroxide solution.

The total volume or weight of the distillate is ascertained, and the acetic acid content is estimated according to the method described under "Analysis of Pyroligneous Acid," page 386; if necessary, the wood-naphtha may also be estimated (see p. 389).

The residue in the flask consists of dehydrated tar which still contains the whole of the tar-oils (apart from a certain proportion of the light oils) and the pitch.

If it is desired to estimate the tar-oils and pitch in addition to the aqueous components (water, acetic acid and naphtha), a larger quantity of tar must be distilled, the process being carried out exactly as indicated by the diagram on page 352.

In cases where a complete examination of the tar is frequently required, it will be found advisable to provide a special apparatus consisting of a small cast-iron still of about 5 litres' capacity, which is connected with a copper coil-condenser. In the first place the pyroligneous acid is distilled over, the light oils which accompany it are separated, and the *weight, acetic acid content and naphtha content* of the pyroligneous acid are determined. The *light oils* are weighed, and their acetic acid content is ascertained, most suitably by titration with a standard alcoholic solution of potassium hydroxide.

The oils which distil over after the pyroligneous acid and light oils are collected in two separate fractions, according to whether they are lighter or heavier than water, and each fraction is weighed.

The distillation is continued, and samples of the pitch are withdrawn from time to time, until it is found to have reached the desired consistency; the process is then complete.

The two fractions of oils mentioned above are redistilled separately, in order to eliminate dissolved tar. The pyroligneous acid which separates from the distillate in each case is

added to the main bulk of the acid which distils over in the first stage of the process, and the acetic acid content of the residual oils is determined by titration with a standard alcoholic solution of potassium hydroxide. The oils are then de-acidified by washing with sodium carbonate solution, the resulting acetate solution is separated, and the *middle oils*, which constitute the main bulk of the fraction lighter than water, are weighed. The *heavy oils* are treated in a separating funnel with a 6 per cent solution of sodium hydroxide until no more phenols can be extracted.

The residual oil consists chiefly of hydrocarbons; the soda solution contains all substances of a phenolic nature which were originally present in the oils. The soda solution is placed in a separating funnel and acidified with mineral acid; the liberated phenols are then separated from the sodium sulphate or sodium chloride solution, redistilled and weighed.

By operating in the above manner it is possible to estimate all the more important components of the tar, including

- Acetic acid,
- Wood-naphtha,
- Light tar-oils,
- Middle tar-oils,
- Heavy tar-oils,
- Phenol content of the tar-oils,
- Pitch,
- Gases and loss.

Moreover, the process of separation is practically identical with that used on the large scale.

2. Examination of Tar-Oils from Hardwood-Tar.—As mentioned above, only a few wood-distillation factories carry on the manufacture of creosote.

Such factories, in order to ensure a sufficiently large output, are compelled to draw on other factories for suitable raw material. In these conditions, the product purchased consists almost invariably of tar-oils and not beechwood tar, which is the usual raw material for the manufacture of creosote. The composition of these oils may differ widely, according to the manner in which the distillation of the tar has been carried out.

The examination of the tar-oils for the purpose of obtaining comparative figures includes :—

- i. Determination of the boiling range and simultaneous

estimation of the tar content of the oils by weighing the residue after distillation.

2. Determination of the specific gravity of the tar-free distillate.

3. Determination of the percentage content of components distilling between 170° and 220° C.

4. Determination of the phenol content of the tar-free distillate, by shaking 20 c.c. of the tar-oil with 40 c.c. of 10 per cent sodium hydroxide solution in a graduated cylinder, allowing to settle, and noting the increase in volume of the soda solution.

These data will provide sufficient information as to the suitability of a particular tar-oil for the manufacture of creosote.

3. Softwood-Tar.—In the great majority of cases, *hardwood-tar* is utilised in the factory of origin, either as a fuel or for distillation. *Softwood-tar*, on the other hand, forms an important article of commerce, the Russian, Swedish and Finnish brands, especially, having a high market value.

An expert judges the value of softwood-tar simply by its appearance and by spreading it on a smooth piece of wood, which should be as nearly white as possible. The lighter the smear, the more sticky it is, the quicker it dries, the smaller the amount of water which it gives off and the more resistant it is to the solvent action of water, the higher is the value of the tar in question. No particular purpose is served by carrying out distillation tests with softwood-tar, since it is never specified that the tar should contain certain definite fractions.

Softwood-tar of good quality should possess a resinous odour. In thin layers it should transmit brownish-yellow light, and it should possess a similar colour when thinly spread on wood. Under the latter conditions it should dry quickly and not darken subsequently, and it should be sufficiently viscous to adhere to the wood without at the same time being difficult to spread.

It is obvious that in order to fulfil these requirements the tar must be as free as possible from pyroligneous acid.

The carbonisation process seldom furnishes directly a tar of the above nature. As a rule, a product of suitable consistency is only obtained by dehydrating the crude tar with steam (see p. 358). The process examination of the softwood-tar is confined almost entirely to observing the appearance of

a smear, the plasticity of the product, time required for drying, covering power, and resistance to the action of water.

4. Crude Pine-Oil.—Crude pine-oil, if produced on an industrial scale, is usually refined in the factory of origin. On the other hand, the pine-oil manufactured by the Russian, Swedish, Finnish and Polish peasants in small factories worked on comparatively primitive lines is sold just as it is produced by the simple type of oven employed. In this case the product must be worked up into the finished article in special refineries.

Obviously, crude pine-oil which is produced in so many different ways must exhibit very great variation in its composition.

The essential components of crude pine-oil are :—

Softwood-tar,

Terpenes, sesquiterpenes, etc.,

Hydrocarbons,

Acetic acid,

Components of wood-naphtha,

Certain substances which impart the characteristic pungent odour to the pine-oil. These substances are tabulated on page 360.

The refiner who purchases crude pine-oil is naturally interested solely in the content of substances which, when extracted from accompanying impurities, will form a product resembling as nearly as possible in physical properties the genuine American oil of turpentine.

For this reason, the examination of crude pine-oil cannot be carried out on a strictly scientific basis. The method of analysis must follow the general lines of the treatment to which the crude product is submitted in the factory, in order that some idea may be gained as to the probable yield of refined pine-oil.

According to the author's experience the best method of assaying crude pine-oil in the laboratory is the following :—

Apparatus :—

A. A steam generator of any suitable type fitted with a pressure tube.

B. A flask of 1500 c.c. capacity which is capable of containing 1 kilo. of the raw material ; it is fitted with a cork bored with five holes, and is heated by means of an oil bath.

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A is connected with *B* by means of a delivery tube, drawn out to a fine point, which reaches nearly to the bottom of *B*. A safety tube is inserted through another hole in the cork, which is also fitted with a tube connecting flask *B* with flask *C*, a thermometer which reaches nearly to the bottom of *B*, and a tube connecting *B* directly with a Liebig condenser *F*.

C and *D* are flasks of 1000 c.c. capacity which are also heated by oil baths.

E is a Liebig condenser which is connected with *D*.

b and *c* are pinchcocks which serve to bring *B* into communication with *F* and *C* respectively.

In carrying out the analysis, 1000 grams of crude pine-oil are weighed into the tared flask *B*, and 300 c.c. of 5 per cent sodium hydroxide solution are placed in each of the flasks *C* and *D*; *b* is left open and *c* is closed. The steam generator *A* is heated to boiling, and the oil baths are also heated.

Oil bath *B* is heated to 150–160° C. and the whole of the distillate which comes over up to that temperature condenses in *F* and is collected in a weighed receiver.

The heating is continued until the contents of *B* have reached a temperature of 150° C. (about 170° C. in the oil bath), which is maintained until distillation ceases. *b* is then closed, *c* is opened, and steam is passed into *B* from *A*.

The temperature in *B*, *C* and *D* respectively must be kept sufficiently high to prevent condensation of the steam and to maintain the liquid in the flasks at an approximately constant level. The distillate flowing from the condenser *E* is collected in a series of graduated measuring cylinders. If the above quantity of raw material is taken, about six fractions, each containing approximately 150 grams of oil, are collected. In each case, the water is separated from the oil, and the weight of the latter is then ascertained.

The distillation is continued until the distillate contains only small traces of oil.

The residue in *B*, consisting of tar, is weighed, and from the figure obtained the tar content of the crude pine-oil is calculated. The weight of each separate fraction is also ascertained, and from the total weight of the fractions plus the weight of tar remaining in *B*, the loss on rectification (phenols, aldehydes, volatile acids, etc.) can be calculated.

The specific gravity and the boiling range of each fraction,

including that collected from condenser *F*, are also determined. The data obtained in this way afford sufficiently reliable information as to the yield of refined pine-oil, boiling over the same range of temperature as oil of turpentine (about 155–180° C.), which may be expected from the large-scale refining process: these data also indicate the probable yields of low-boiling fractions distilling below 150° C., as well as of the products which boil above 180° C. and which may be regarded as lower grades of pine-oil.

If comparative data are required in respect of samples of *refined pine-oil*, it is usual to make the following determinations :—

1. Residue after evaporation on a water bath.
2. Specific gravity.
3. Boiling range, with special regard to the proportions distilling below 150° C. and above 180° C. respectively.
4. Colour and odour.
5. Optical rotation.

The various fractions obtained in carrying out the examination of *crude pine-oil* by the above method do not, of course, represent finished commercial products. These fractions are certainly free from phenols, volatile acids, and the main bulk of the aldehydes, but their odour is not yet satisfactory.

The objectionable odour is only eliminated by repeated chemical treatment of the distillate and careful rectification in column stills.

The above method, however, furnishes valuable comparative data in respect of the three fractions :—

1. Boiling below 150–155° C.
2. „ between 150–180° C.
3. „ above 180° C.

W. C. Geer¹ describes a method for the fractional distillation of oil of turpentine, or pine-oil, in which a special form of still-head, constructed of glass on the principle of a column still, is used. Judging by the accompanying diagrams, this apparatus effects a good separation of the components of pine-oil.

¹ "The Analysis of Turpentine by Fractional Distillation with Steam"; U.S. Department of Agriculture, Forest-Service Circular, 152 (Washington, Government Printing Office). See also Allen's "Commercial Organic Analysis" (London, 1911, J. and A. Churchill) Vol. IV, p. 419.

In this connection, however, the principle of steam-distillation is comparatively old, since the method described above was employed by the author many years ago for judging the various qualities of pine-oil.

It is possible, by means of the technical methods employed for refining crude pine-oil, to obtain fractions which are water-white, have a mild and perfectly pleasant odour, leave no residue on evaporation, and possess the same boiling point, specific gravity and optical rotation as the genuine oil of turpentine which is obtained by the steam-distillation of "turpentine" (the mixture of rosin and oil of turpentine which flows spontaneously from coniferous trees). At the same time, some difference always exists between genuine oil of turpentine and the product derived from the destructive distillation of richly resinous coniferous wood.

A useful standard with which to compare the various fractions of pine-oil during the process of refinement is the following specification for genuine oil of turpentine issued by the Bureau of Supplies and Accounts, Navy Department, U.S.A. :—

1. The oil of turpentine must be a distillate properly manufactured from suitable varieties of pitchpine; it must not be mixed with any other products whatsoever. It should be a pure, clear, water-white liquid possessing a sweet odour.

2. A drop, when placed on white paper, must evaporate completely at 20° C. without leaving any stain.

3. The specific gravity at 15° C. must not be less than 0.862 or more than 0.872.

4. On distillation, not less than 95 per cent of the oil of turpentine must pass over between 153° C. and 165° C., and the residue must consist only of the heavy components of pure oil of turpentine.

5. A known quantity of the oil of turpentine is evaporated in an open dish at the temperature of the water bath. If the residue amounts to more than 2 per cent of the original quantity taken, the oil of turpentine will be rejected.

6. *Flash Point*.—An open assay crucible is filled to 6.4 mm. of the brim with the oil of turpentine, which may be taken from any one of the containers in which the product has been supplied. The crucible containing the oil is allowed to float on water contained in a metal dish. The water is heated gradually,

but uniformly, so that the temperature—beginning at 15° C.—rises 2° F. per minute. The taper should consist of fine linen- or cotton-twine (which burns with a uniform flame) and should not have been impregnated with any substance. As soon as the temperature has risen to 38° C., the lighted taper is passed horizontally, at the same level as the brim of the crucible, over the surface of the oil of turpentine, and this operation is repeated at every 1° F. rise in temperature. The temperature is read on a thermometer which is so placed that the bulb is completely covered by the oil of turpentine in the crucible. The oil of turpentine must not flash below 41° C.

7. *Sulphuric Acid Test*.—6 c.c. of the oil of turpentine are placed in a stoppered cylinder of 30 c.c. capacity, graduated in tenths; the cylinder is then filled to the highest graduation mark with concentrated sulphuric acid.

The cylinder is cooled, the stopper is replaced, and the contents are thoroughly mixed by shaking, during which the cylinder is cooled if necessary with water. The cylinder is allowed to stand at room temperature for not less than half an hour, and the amount of undissolved oil is then noted. If more than 6 per cent of the sample remains undissolved in the acid, the oil of turpentine will be rejected.

The more nearly a refined pine-oil conforms to this specification, the purer it is and the more closely does its price approach that of genuine oil of turpentine.¹

(p) Examination of Charcoal.

As a general rule the quality of charcoal is judged simply by its external characteristics (see p. 74), especially if the product is intended for small-scale industrial operations, as is usually the case.

If the charcoal is intended chiefly for domestic purposes (as kitchen fuel, for heating laundry irons, etc.), as is generally the case in Southern countries, it is essential that the product should burn without odour. Hence, in addition to the ordinary superficial examination, the charcoal must undergo a combustion test, which is carried out by placing an average sample on a perforated pan, resting on a tripod, and igniting it. The charcoal should burn without odour and without emitting sparks.

¹ Further information on the analysis of wood-turpentine and pine-oil may be found in U.S. Forest Bulletin 105, and U.S. Agriculture Bulletin 898.

A high-grade charcoal is quickly recognised by its property of burning without odour, its characteristic metallic note, its colouring power, and its property, in small pieces, of adhering to the tongue.

If the charcoal is intended for metallurgical purposes, its quality is judged from quite another point of view. In this case, the main requirements are high carbon-content and therefore a relatively low content of hydrogen and oxygen.

In this connection, the methods used for testing the quality of the charcoal are those which are applied to fuels in general, namely, determination of the calorific value and, if necessary, ultimate analysis of the product. It will be taken for granted that the methods of performing this analysis and likewise the method of using the calorimeter are known to the reader.

In Chapter VIII, attention has already been called to the fact that charcoal which has been produced at a certain definite temperature exhibits an almost constant chemical composition—the latter being represented by the formula $C_{30}H_{18}O_4$ —as shown in the following table:—¹

Origin.	Carbon. Per cent.	Hydrogen Per cent.	Oxygen. Per cent.	Ash. Per cent.	Yield : Charcoal from moisture-free wood. Per cent.
Charcoal $C_{30}H_{18}O_4$	81.5	4.1	14.5	—	—
Carbo-ovens	79.0	4.5	15.4	1.1	—
"	82.1	4.1	13.0	0.8	—
"	81.2	4.1	13.7	1.0	—
"	80.9	4.4	13.7	1.0	—
"	80.8	4.1	14.2	0.9	43.5
Pipe-ovens	79.5	4.5	15.0	1.0	42.4
Gröndal retorts	81.5	4.1	13.4	1.0	—
Cellulose, spruce	81.32	4.23	14.45	—	34.86
" Scotch pine	81.69	3.64	14.07	—	36.93
" cotton	81.79	3.89	14.34	—	38.82
" birch	83.7	4.3	12.0	—	33.39
" beech	83.1	4.1	12.8	—	32.91

The above formula only applies when the end-temperature in the carbonising apparatus is about 400° C.

¹ Cf. *Klason, von Heidenstamm and Norlin, Zeit. angew. Chem.*, 1909, **22**, 1205.

If charcoal which has been produced at 400°C . is heated to a higher temperature (e.g. 500° or 600°C .), it will still give off volatile matter; it follows therefore that in determining the amount of volatile matter in charcoal which has been manufactured in the ordinary type of carbonising apparatus, the sample must not be heated above 400°C .

In addition to the carbon-content, general elementary composition, ash-content, and individual components of the ash, the metallurgist is naturally interested in the amount of carbon contained in a given volume of stick charcoal.

If the weight of a bulk-measure (e.g. 1 cu. metre in pieces of normal size) of charcoal used for smelting purposes is relatively low, it follows that a smaller number of units of carbon is being introduced into the available space of the blast-furnace than when the above weight is relatively high.

According to Juon¹ the specific gravity of the charcoal substance, free from pores—that is, in the form of powder—is the same for practically all kinds of charcoal. On the other hand, the specific gravity of individual pieces of charcoal—that is, of the charcoal substance together with the pores, which are characteristic of the structure of the material—shows considerable variation.

For example, the specific gravity of *powdered air-free charcoal* derived from

White spruce	=1.38
Common spruce	=1.40
Birch	=1.46

whereas the specific gravity of pieces (cubes) of charcoal including the pores, derived from

White spruce	=0.215
Common spruce	=0.270
• Birch	=0.400

The weight of a bulk-measure of charcoal also varies; for example, 1 cu. metre of charcoal from

White spruce	weighs	131	kilos.
Common spruce	„	148	„
Birch	„	190	„

¹ Loc. cit.

Naturally these figures are not always free from error; on the other hand, it is possible to determine with accuracy the specific gravity of a single cube of charcoal.

The latter determination is carried out, according to Juon, by cutting out a cube from the piece of charcoal under examination, weighing it, and then coating each side thoroughly with paraffin wax. The cube is then weighed on a hydrostatic balance. The error which is introduced owing to the slightly different specific gravity of the paraffin wax is negligible. Juon states that this method gives practically the same result as the determination of the specific gravity by purely scientific methods, which, of course, are much more complicated.

Knowing the specific gravity of a charcoal cube, the results of ultimate analysis, the ash-content, and the mechanical resistance to crushing, the metallurgist can judge the quality of a sample of charcoal with certainty.

In addition to the above data, the moisture-content and the amount of volatile matter present are very frequently of interest.

The *moisture-content* is determined by drying a weighed quantity of powdered charcoal at $120^{\circ}\text{C}.$, and the *volatile matter* by heating to $400^{\circ}\text{C}.$ The latter determination is best carried out in an air bath, the temperature being controlled by means of an ordinary or electric pyrometer.

Below $400^{\circ}\text{C}.$ no considerable loss should occur; otherwise, it is an indication that the charcoal has been produced below the normal end-temperature, and that probably the carbon-content is too low. In this test, charcoal which has been produced under normal conditions loses, at the most, not more than 5 per cent, apart from moisture. •

CHAPTER XXI

RECENT PROGRESS

On reviewing the history of wood distillation covering the past ten years it is difficult to point to any very striking advances in the technology of the process. Improvements in plant have consisted more in refinements than in the introduction of new principles, and have been directed chiefly to the various forms of apparatus utilised in working up the crude pyroligneous acid to the finished commercial products.

New processes of dealing with small waste wood and similar material have appeared, and several are being worked on a commercial scale. In most cases, however, details as to yields and costs of operation are not yet available, and it is probably still too soon to decide whether any of these processes can be looked upon as having finally overcome the difficulties connected with the carbonisation of small waste material and already mentioned in Chapter XII.

On the other hand, much useful research work on the nature of the process and the composition of the raw material has been accomplished, and the results, if at present only of scientific interest, may later find application on the commercial scale.

The development of forestry in tropical and semi-tropical countries, and particularly in the British Dominions, has naturally led to the consideration of the possibilities of utilising wood waste in various ways, and to an examination of the prospects of founding a wood-distillation industry in the countries concerned. As a result many different species of wood and other cellulosic material have been investigated during the past few years in regard to their suitability for the process of destructive distillation, and a large mass of data in respect of yields of products is now available. With this information it is possible—within the limits mentioned in Chapter IV—to compare the value of these lesser-known species with that of the European and American woods most frequently utilised

for distillation and for which the yielding capacity is reasonably well established.

NEW FORMS OF CARBONISING APPARATUS

Of recently introduced processes, involving the use of new types of carbonising apparatus to deal with small waste, the following are probably of greatest interest :

The Seaman Process.¹—This is a continuous process and makes use of an inclined rotary retort fitted internally with blades for agitating the charge. The main feature is the elimination of air from the raw material, just before its entry into the retort, this being effected by means of a ram which highly compresses the material as it falls from a hopper into the feed pipe. At the same time the compressed mass forms a seal which prevents the escape of the volatile products from the retort. A similar ram is provided at the discharge end of the retort, making it possible to remove the charcoal continuously without simultaneous loss of gas and vapour.

This process is reported to be successful commercially and to give high yields of acetic acid and wood-naphtha, and a charcoal of particularly good quality.

The Stafford Process.²—This process depends on the utilisation of the heat developed by the exothermic reaction to raise the temperature of the fresh incoming wood to the exothermic point. The raw material is dried and heated in the first place, and is then delivered into the retort which is of very simple construction, consisting essentially of a large well-insulated vertical chamber. During operation a thick bed of charcoal is kept in the bottom of the retort, and charcoal can be discharged either continuously or intermittently by means of suitable valves or plugs. One of the chief features of this process is the elimination of all moving parts, such as conveyors and scrapers, from the interior of the retort.

Owing to the rapid heat exchange between the freshly charged dry material and the hot vapours, no stirring or agitating apparatus is necessary, and once the retort is in full operation no further application of heat from outside sources is required. Assuming that the drying and preheating of the raw material can be effected at a reasonable cost, this process would appear to offer distinct advantages compared

¹ U.S. patent 1,236,885 (1917).

² U.S. patent 1,380,262 (1921).

with the various forms of plant previously employed for the carbonisation of small waste.

FURTHER DATA ON YIELDS OF PRODUCTS

The difficulty of obtaining exact figures for yields of products has already been emphasised in Chapter IV; and recent work on this subject fully confirms those statements. In this connection a series of investigations by Hawley and Palmer¹ are particularly interesting. The experiments were carried out in a small horizontal cylindrical retort heated by an oil-jacket. Temperature measurements were made by means of pyrometers placed at different points placed in the retort, and the conditions for the whole series of tests were kept as uniform as possible.

As a result of these investigations a comparison of yields was obtained for various forms of wood (heartwood, slabs, and in some cases bark and sapwood), and it was also possible to show that these yields varied considerably according to the locality from which the wood was derived.

The following table gives the yields of acetic acid and wood-naphtha, calculated on moisture-free wood, for a number of species of American hardwood:—

Species.	Locality.	Wood-naphtha, 100%.			
		Heart-wood. %	Slab-wood. %	Mean heart and slab %	Other forms. %
Beech	Indiana	1.95	1.79	1.87	{ Bark 1.25 Sapwood 1.97
"	Pennsylvania	2.23	2.09	2.16	
Birch	Wisconsin	1.45	1.55	1.54	
"	Pennsylvania	1.62	1.59	1.60	
Maple	Wisconsin	1.94	1.91	1.93	Bark 1.88
"	Pennsylvania	1.94	1.78	1.86	
Chestnut	New Jersey	0.90	0.87	0.89	Limbs 0.96
White oak	Indiana	1.34	1.33	1.33	
" "	Arkansas	1.33	1.46	1.39	

¹ U.S. Dept. Agr. Bulletins, 129 and 508.

Species.	Locality.	Total Acetic Acid.			
		Heart-wood.	Slab-wood.	Mean heart and slab	Other forms.
		%	%	%	%
Beech	Indiana	5.56	6.18	5.87	{ Bark 2.98 Sapwood 6.67
"	Pennsylvania	5.77	6.21	5.99	
Birch	Wisconsin	6.71	6.88	6.80	
"	Pennsylvania	6.19	6.10	6.15	
Maple	Wisconsin	5.42	5.11	5.24	Bark 3.15
"	Pennsylvania	5.66	5.44	5.55	
Chestnut	New Jersey	5.50	5.26	5.36	Limbs 6.42
White oak	Indiana	4.97	4.77	4.87	
" "	Arkansas	4.23	4.35	4.29	

These figures are of considerable importance from the commercial point of view. Apart from indicating the relative values of the various species for distillation, they also show that, as far as the yields of acetic acid and naphtha are concerned, a high percentage of sapwood in the raw material is not necessarily a disadvantage as is often assumed. For example, the sapwood of beech gives practically the same yield of naphtha as the heartwood, and a distinctly higher yield of acetic acid. The yield of naphtha from beech slabwood, which consists mainly of sapwood and bark, is not as favourable as that from the heartwood, on account of the relatively low yield from the bark; on the other hand, owing to the superior yielding capacity of the sapwood, the slabs may contain as much as 13 per cent of bark and still give more acetic acid than the heartwood.

For maple (Wisconsin) the relations are different. In this case the yield of naphtha from the bark is almost as high as from the heartwood; consequently the yield of naphtha from the slabwood is nearly equal to that from the heartwood. As far as acetic acid is concerned maple sapwood would appear to be less favourable than beech in relation to the heartwood, since the slabwood gives a lower yield than the heartwood, although the bark yields more acid than beech bark.¹

¹ It is assumed of course that the proportion of bark in the slabwood is the same in each case.

	Char- coal. %	Acetic Acid. %	Methyl Alcohol. %	Tar. %
<i>Acacia catechu</i> . . .	45.6	2.73	1.29	5.8
<i>Adina cordifolia</i> . . .	35.9	3.14	1.67	9.8
<i>Albizzia amara</i> . . .	32.7	2.42	1.28	7.9
<i>Anogeissus latifolia</i> . . .	40.5	4.24	1.51	9.6
<i>Anthocephalus cadamba</i> . . .	42.6	3.02	1.77	8.3
<i>Bassia latifolia</i> . . .	36.9	3.05	1.13	7.4
<i>Bassia malabarica</i> . . .	40.4	3.05	2.08	8.3
<i>Bauhinia racemosa</i> . . .	44.2	3.76	1.27	10.0
<i>Bridelia retusa</i> . . .	42.2	3.12	1.20	6.6
<i>Buchanania latifolia</i> . . .	40.9	3.54	1.43	10.5
<i>Careya arborea</i> . . .	42.4	3.34	1.42	8.0
<i>Cassia fistula</i> . . .	43.6	3.39	1.57	10.9
<i>Casuarina equisetifolia</i> (old)	36.8	4.86	1.52	8.1
" " " (young)	38.7	3.94	1.67	9.1
<i>Chloroxylon swietenia</i> . . .	37.2	2.61	1.32	12.0
<i>Dalbergia latifolia</i> . . .	40.6	3.02	2.21	13.0
<i>Dillenia pentagyna</i> . . .	41.8	3.75	1.48	8.2
<i>Diospyros tupru</i> . . .	42.0	2.97	1.53	6.8
<i>Elæodendron glaucum</i> . . .	37.3	4.47	1.43	9.9
<i>Eucalyptus globulus</i> . . .	32.0	3.95	1.64	6.4
<i>Eugenia jambolana</i> . . .	40.8	3.18	1.19	6.8
<i>Garuga pinnata</i> . . .	42.4	4.94	2.28	8.4
<i>Gmelina arborea</i> . . .	35.3	3.19	1.20	8.6
<i>Grewia tiliaefolia</i> . . .	39.2	3.20	1.89	8.5
<i>Holarrhena antidysentrica</i> . . .	37.3	2.48	1.26	5.6
<i>Holoptelia integrifolia</i> . . .	39.5	2.74	1.23	8.3
<i>Ixora parviflora</i> . . .	38.0	3.45	1.26	8.6
<i>Lagerstroemia lanceolata</i> . . .	46.2	3.17	1.39	7.4
<i>Lagerstroemia parviflora</i> . . .	37.6	2.61	0.85	8.0
<i>Mangifera indica</i> . . .	38.5	2.75	1.67	8.8
<i>Phyllanthus emblica</i> . . .	40.4	3.53	1.52	6.8
<i>Pongamia glabra</i> . . .	35.9	4.10	1.49	9.2
<i>Pterocarpus marsupium</i> . . .	41.5	3.25	1.69	7.4
<i>Saccopetalum tomentosum</i> . . .	32.0	2.58	1.19	6.7
<i>Schleichera trijuga</i> . . .	40.0	3.01	1.89	9.5
<i>Shorea talura</i> . . .	44.7	3.59	1.39	7.3
<i>Stereospermum suaveolens</i> . . .	36.3	3.60	2.16	11.8
<i>Tamarindus indica</i> . . .	37.5	3.95	1.89	12.7
<i>Tectona grandis</i> . . .	38.8	3.52	1.67	11.1
<i>Terminalia belerica</i> . . .	33.0	3.08	1.78	7.8
<i>Terminalia paniculata</i> . . .	45.0	2.94	1.07	6.9
<i>Terminalia tomentosa</i> . . .	45.5	2.62	1.33	5.8
<i>Vitex altissima</i> . . .	40.3	2.79	1.32	9.9
<i>Xylia dolabriformis</i> . . .	47.3	2.76	1.32	5.5
<i>Ziziphus xylopyrus</i> . . .	43.0	3.50	1.35	9.2
" " " . . .	39.0	3.70	1.32	10.1

As yet only very few species have been examined completely on the above lines, but it is to be hoped that these investigations will be continued until sufficient data are available for a comparison not merely of the various species, but also of the different parts of the same species, in regard to their value for distillation.

A considerable amount of small scale investigation has recently been carried out on Indian woods.¹ The table on p. 473 gives the yields, calculated on the moisture-free wood, for forty-six South Indian species. Only the botanical name is given here as the vernacular name differs in different parts of the country.

It will be seen from the other figures that the yields of acetic acid and naphtha are generally inferior to those from the European and American hardwoods. The best wood is *Garuga pinnata* which gives 4.94 per cent of acetic acid and 2.28 per cent of naphtha. Casuarina, which gives a relatively good yield of acetic acid, is actually being used for large-scale operation in India.

In Chapter II reference is made to the use of materials other than wood for distillation. In this connection Sudborough² investigated several Indian waste-products with the results shown in the following table :—

	Char- coal. %	Acetic Acid. %	Wood- naphtha. %	Tar. %
Cocoanut shells	41.5	6.80	1.32	6.8
Wattle	39.4	5.87	1.97	7.3
"	34.7	6.03	1.42	10.6
Sur reed	42.6	4.17	0.64	6.1
Myrabolan kernels . . .	45.5	4.75	0.89	7.8
Gold mohur husks . . .	42.8	4.45	1.20	7.1
Bamboo :	41.3	4.34	1.65	7.9

The above yields are calculated on the moisture-free material.

Cocoanut shells not only give a particularly good yield of acetic acid, but produce a charcoal of high quality.

¹ Watson and Sudborough, Journ. Ind. Inst. Sci., Vol 2, Part VII, p. 79 (1918), and Vol. 3, Part IX, p. 281 (1920).

² Loc. cit.

One of the main difficulties in turning these materials to commercial account is the cost of collection, especially in countries where the degree of development is still relatively low. A good example of this difficulty is afforded by the Malabar coast of India which is one of the richest cocoanut-growing regions in the world. The chief product of the nut is copra, but the extraction of this material is a village industry scattered over a very wide area and not centralised at the mills where the copra is subsequently crushed for oil. Consequently, to obtain a sufficient supply of shells for distillation on a reasonable commercial scale would necessitate organised collection and transport, which may in certain circumstances prove costly items. Apart from this fact, the shells are used largely as fuel in the native villages and their price would often be regulated by the price of substitutes.

Another difficulty attaching to the use of such materials as bamboo and sur reed is their low density. Unless the material were compressed, thus adding to the cost, the utilisation of the retort space would be poor, and the performance of the plant relatively low.

Wattle waste seems to offer better possibilities. Large quantities of this material are available in India, since the extraction of the bark for tannin is an important industry in that country. The Imperial Institute¹ has examined the black wattle of British East Africa and has shown that the yields from this wood are at least as good as those from oak, but are inferior to those from birch, beech and maple.

In connection with the distillation of waste materials of the above nature it is safe to say that, however attractive the material may appear to be from the point of view of prime cost and yields, these factors are often of much less importance than problems of transport, labour and markets for the products; consequently, without a very thorough knowledge of local conditions and general facilities for carrying on the industry, it is impossible to judge whether a scheme for the utilisation of any of these waste materials by distillation is a reasonable commercial proposition.

The suitability of Australian woods for distillation has also received attention and the Australian Forestry Commission has recently published the results obtained on the small

¹ Bull. Imp. Inst., Vol. xiv, 4, 571.

scale for a number of species occurring in New South Wales.¹ Two of the best-known species—jarrah and karri—gave the following figures, calculated on a moisture-free basis:—

	Charcoal. %	Acetic Acid. %	Naphtha (100%). %	Tar. %
Jarrah . . .	41.4	1.87	1.61	5.9
Karri . . .	37.4	3.03	1.71	5.7

It is stated that the wood used for these tests was probably very old.

Poore and Rule examined jarrah and karri sawdust and another Australian wood—white stringybark—with the following results:—

	Charcoal. %	Acetic Acid. %	Naphtha (100%). %
Jarrah sawdust . . .	46.5	2.23	0.90
Karri sawdust . . .	46.2	2.88	1.29
White stringybark . .	38.6	3.48	1.71

There are some considerable differences amongst the two sets of figures, but it is obvious that the yields of acetic acid from these woods are very poor compared with those from the standard European and American species. It is interesting to note that the yields from stringybark show remarkable agreement with those from Indian teak (*Tectona grandis*: p. 473); in fact, as far as value for distillation is concerned, the above species appear to be of the same order as the majority of the Indian woods.

Whilst dealing with the subject of yields it may be pointed out that only comparatively rarely is it possible to confine the process to the distillation of one particular species. If virgin forests are being exploited it may be possible to select only those species which afford the best yields, and still to obtain sufficient supplies of material for carrying out the

¹ Commonwealth of Australia, Inst. Sci. Ind., Bull. 19.

industry on a considerable scale. In countries such as Great Britain, however, where a factory may have to depend largely on cordwood from mixed plantations, yields may vary widely.

An English factory with modern equipment, working on well-seasoned cord- and slabwood consisting for the most part of varying proportions of the higher-yielding species such as beech, birch and oak, may be expected to produce on a yearly average the following amounts of products *per 100 tons of wood carbonised* :—

	Tons.
Charcoal	25.5
Grey acetate of lime (80%)	5.0
Wood-naphtha (100%)	1.1
Tar	4.2

POSSIBILITIES OF INCREASING THE YIELDS OF ACETIC ACID AND METHYL ALCOHOL

During the last decade a large amount of investigation has been carried out in an attempt to arrive at a closer knowledge of the composition of wood. In this field undoubted progress has been made; in addition, various methods have been devised for the qualitative determination of the different constituents. At present, however, it is impossible to point to any very close connection between the composition of the wood, as determined by chemical analysis, and the yields of the distillation products obtained when the wood is carbonised.

Further investigation may provide us with data from which we can deduce whether it is reasonable, given suitable conditions, to expect greater yields of acetic acid and methyl alcohol than the highest which have been obtained so far from the different species of wood. For example, it is assumed that the methyl alcohol appearing as a distillation product is derived from methoxy groups present in the lignin. Schorger¹ gives the following table showing the relative percentages of methoxy

¹ Journ. Ind. Eng. Chem., 1917, 9, 556.

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(OCH₃) in various woods, and the methyl alcohol obtained by destructive distillation :—

	Birch.	Maple.	Larch.
Methoxy (per cent of dry wood)	6.07	7.25	5.03
Methyl alcohol (per cent of dry wood)	1.53	1.94	0.65

From these figures it is obvious that under the ordinary conditions of carbonisation a large proportion of the methoxy in the lignin either remains unchanged or else reacts to form compounds other than methyl alcohol. Moreover, it is also clear that the relatively low yield of methyl alcohol from the softwood, compared with the hardwoods, is not due to a correspondingly lower content of methoxy groups. A practical method of increasing the conversion of methoxy into methyl alcohol would represent an important advance from the commercial point of view, since methyl alcohol is a very valuable product of the wood-distillation industry.

Recent work has shown that it is possible in various ways to increase the yield of products, but few of these methods are applicable to the large scale process. One of the most important series of investigations in this connection is that made by Palmer¹ on the effect of controlling the temperature during the distillation process. In earlier chapters the various stages of the process have frequently been described, and the necessity of preventing the carbonisation from becoming too violent during the exothermic period has repeatedly been emphasised.

Palmer carried out his experiments on the laboratory scale in a small cylindrical retort surrounded by an oil jacket. Temperature measurements were made by means of pyrometers placed at three different points in the retort. In one case the wood was carbonised as rapidly as possible; in the other case the process was controlled in the sense that the largest possible part of the distillation was conducted at the lowest possible temperature, the rate of rise of temperature being kept at a minimum during the exothermic period.

The following table shows the effect of controlling the

¹ Journ. Ind. Eng. Chem., 1915, 7, 663.

temperature on the yields of wood alcohol and acetic acid for maple, beech and birch :—

	Yield of Wood Alcohol.		Yield of Acetic Acid.	
	Uncontrolled % of dry wood.	Controlled % of dry wood.	Uncontrolled % of dry wood.	Controlled % of dry wood.
Maple	1.59	2.31	5.65	5.76
Beech	2.04	2.15	5.77	6.28
Birch	1.63	1.75	6.54	6.87

Palmer then investigated the effect of temperature control in a large scale retort, and employed four different methods of firing the retort, viz. :—

1. Rapid firing throughout the run.
2. Slow firing during the drying period ; rapid firing during the exothermic period to the end of the run.
3. More rapid firing during the drying period, but slower firing during the exothermic period than in 2.
4. Rapid firing during the drying period ; slow firing during the exothermic period.

A charge of $4\frac{1}{2}$ cords (about 7 tons) of wood, consisting mostly of maple, was employed in each trial. The following table gives the yields obtained as a result of firing the retort according to the above methods :—

Method.	• Wood alcohol, 95%.		Acetate of lime, 80%.	
	Gals. per cord.	% increase over method 1	Lbs. per cord.	% increase over method 1.
1	8.2	—	187	—
2	9.62	17.3	194.5	4
3	9.93	21.1	209	11.8
4	10.66	30	213.6	14.2

From these figures it is obvious that method 4 is the most advantageous. In operating according to this method the

firing is carried out rapidly until the first signs of tar appear in the distillate, this point being reached sometime before the regular flow of tar begins. The firing is then checked, and the rate of rise of temperature during the exothermic stage is kept as low as possible.

Lawrence¹ has also studied the question of temperature control and has shown that as a result of checking the firing of the retort, compared with steady firing throughout, the yield of acetate of lime was increased in one trial by about 25 per cent.

The importance of this method of influencing the yields is that it can actually be applied in practice without the necessity of modifying already existing plant. In many wood-distillation factories, especially those in which comparatively primitive methods of operation are still to be found, it is often considered sufficiently satisfactory if the process can be conducted so that the charge is carbonised in a certain time without the exothermic stage becoming too violent. It would probably repay every wood-distiller who has not already studied this question to experiment with his own plant along the lines indicated in the publications of Palmer and Lawrence, and to endeavour to establish a definite system of firing on which he could rely to give him the best results.

The *effect of pressure* on the course of the distillation process has been studied by Klason² who carried out a series of distillations under reduced pressure. At very low pressures the yield of acetic acid was slightly increased, owing to the fact that under these conditions formation of acetone, which at ordinary pressure is produced by the secondary decomposition of acetic acid, no longer takes place. The effect on the yield of methyl alcohol was only small, a slight decrease being shown under reduced pressure. On the other hand, in vacuum distillation, there was a large increase in the yield of tar, as much as 43.6 per cent being obtained from birch wood in cathode-light vacuum; under the same conditions there was a marked decrease in the yield of charcoal.

Palmer³ investigated the effect of pressures above the atmospheric pressure on the distillation process. Various species and forms of wood were used, and various pressures up to 150

¹ Journ. Soc. Chem. Ind., 1918, 37, 5.

² Journ. prakt. Chem., 1914, 90, 413.

³ Journ. Ind. Eng. Chem., 1914, 890, 6.

lb. per sq. inch were employed. The results in general showed, that with increase in pressure, the yield of acetic acid was decreased considerably, whereas the yield of alcohol was slightly increased. The yield of charcoal was also increased, but the most striking effect was shown in the yield of tar which in the case of birch sawdust decreased from 11.9 per cent at atmospheric pressure to 3.86 per cent at a pressure of 120 lb. per sq. inch.

Klason, as a result of his investigations, has put forward some very interesting views as to the cause of the exothermic reaction and the formation and nature of wood-tar and charcoal under different conditions of operation.

The *influence of moisture* on the yields of products has been further studied by Palmer and Cloukey¹ in a small experimental plant. Controlled and uncontrolled distillation were made with "wet" and "dry" wood, and as a result it was shown that in some cases higher yields of acetic acid and alcohol were obtained with the wetter wood. It is doubtful, however, if these results have any significance for large scale practice since the conditions in a commercial apparatus, especially as regards temperature and velocity of distillation, are very different. In any case, even if it were definitely established that similar results could be obtained on the large scale, this fact would only prove of practical interest if the advantages of distilling wetter wood more than compensated for the cost of evaporating the extra amount of water introduced into the process.

The *effect of treating the wood with chemicals* prior to distillation has received considerable attention, but here again it is doubtful if at present the subject is of more than theoretical interest.

Palmer² made a series of distillations with maple and beech chips which had previously been impregnated with phosphoric acid. Maple, containing 7.59 per cent of the acid, showed a large increase in the yield of alcohol, whereas the yield of acetic acid remained unchanged. Beech, on the other hand, with varying amounts of phosphoric acid (up to 9.7 per cent), gave increased yields of both products.

Hawley³ has since repeated these tests with maple sawdust which was briquetted before distillation. He found that, con-

¹ Journ. Ind. Eng. Chem., 1918, **10**, 262.

² Journ. Ind. Eng. Chem., 1918, **10**, 264.³

³ Journ. Ind. Eng. Chem., 1922, **14**, 43.

trary to Palmer's results, the effect of treatment with phosphoric acid was slightly to lower the yield of alcohol, and slightly to increase that of acetic acid. Hawley was able to confirm Palmer's observation that in the presence of phosphoric acid the yield of settled tar was practically negligible and a large reduction took place in the yield of dissolved tar.

Hawley also examined the effect of other chemicals on maple and white oak;¹ the most interesting results being obtained with sodium carbonate.

Maple blocks, simply soaked in a solution of that reagent and then distilled, already showed an increase in the yield of alcohol. Similar blocks, impregnated with the solution under a pressure of 100 lb. per sq. inch, thus ensuring much better penetration, gave a still higher figure for alcohol; but the best yields were furnished by maple sawdust which had first been soaked in the solution, afterwards briquetted, and then distilled in a special type of apparatus which prevented the briquette from collapsing during the operation.²

Using 1.5 per cent sodium carbonate an increase of 48 per cent in the yield of alcohol was obtained; the yield of acetic acid, however, remained practically the same as for the untreated sawdust. White oak sawdust with 0.5 per cent sodium carbonate showed an increase of 120 per cent in the alcohol yield and a slightly increased yield of acetic acid.

Milk of lime, equivalent to 60 per cent CaO, mixed with maple sawdust, increased the yield of alcohol by 52 per cent, but the yield of acetic acid was greatly reduced. Calcium carbonate, sodium silicate and other reagents were also used with varying results, the effect on the yield of acid being in most cases adverse.

Although no clear explanation can be given for the increase in the yield of alcohol in these tests, Hawley³ has been able to point to a very interesting difference in the distribution of the methoxy groups among the products, as a result of distilling the wood with sodium carbonate.

From the commercial point of view the increase in the yield of alcohol brought about by this method is naturally of great interest, but apart from the cost of the preliminary treatment, the contamination of the charcoal with foreign substances may

¹ *Quercus alba*.

² Journ. Ind. Eng. Chem., 1921, 13, 301.

³ Journ. Ind. Eng. Chem., 1922, 13, 1055.

prove a serious drawback. A soluble salt such as sodium carbonate might be extracted by washing the charcoal with water, but the cost of this operation and subsequent drying would be relatively heavy.

Distillation in the Presence of Superheated Steam. A process of very considerable interest, involving the introduction of superheated steam into the retort during the process of distillation, has been introduced by Poore.¹

The effect of superheated steam on the wood-distillation process had already been investigated to some extent by earlier workers. Violette, in 1848, utilised this agent alone as a source of heat in carbonising wood for the preparation of charcoal of definite quality such as that required for the manufacture of gunpowder. Kahl² also used superheated steam for the same purpose. Later, Hausbrand³ described an apparatus in which the wood was heated from an external source and superheated steam was introduced at the same time directly to the charge. It was claimed that higher yields of products were obtained by this process.

Büttner and Wislicenus,⁴ as a result of a lengthy investigation, showed that on the laboratory scale the use of superheated steam improved the quality of the charcoal and increased the yield of acetic acid by about 10 per cent, but the yield of alcohol was reduced. The experiments were repeated in a small technical experimental plant, but in this case the yields were low and the course of the process appeared to be different on the larger scale.

In the Poore process a cylindrical rotary retort is used. The retort is heated externally by means of a furnace and is fitted internally with perforated pipes for conveying the superheated steam to the charge. When finely divided material such as olive stones or sawdust is being carbonised, an inner tube, specially constructed to prevent dust entering the vapour-pipe, is inserted along the central line of the retort.⁵

Poore has tested many different materials in his apparatus and has been able to show that increases in the yields both of acetic acid and naphtha are obtainable by the use of superheated steam, the extent of these increases depending on the temperature at which the steam is admitted to the charge.

¹ British patent 152,741. ² Dingl. polyt. Journ., 1856, p. 292.

³ Zeitschrift des Vereines deutscher Ingenieure, 1889, p. 228.

⁴ Journ. prakt. Chem., 1909, 79, 183.

⁵ British patent 162,769.

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For each material carbonised there appears to be a definite temperature at which the yields of acetic acid and naphtha respectively reach a maximum; these temperatures may not be identical, but as a rule they lie close together.

The results of a series of tests on olive residues or "grignons" (see p. 37) in the Poore plant may be taken as an illustration of the process.

A charge of 55 lb. of the residues was used for each test. The average moisture-content of the material was about 20 per cent. The average yields of products (excluding tar), from the grignons carbonised without steam in the rotary retort, were as follows:—

	Per cent of moisture-free material.
Charcoal	49.4
Total acid as acetic	4.57
Wood-naphtha (100%)	1.68

In the series of tests with steam the temperature of the latter was kept constant for each test, but was raised step by step throughout the series. The other conditions were kept as nearly as possible the same, and the firing was so controlled as to ensure the same rate of rise of temperature in the retort. The results are shown in the following table, the yields being calculated on the moisture-free raw material:—

No. of test.	Charcoal. Per cent.	Total acid as acetic. Per cent.	Naphtha (100%). Per cent.
1	45.2	4.99	—
2	45.2	5.00	—
3	45.7	5.13	2.11
4	44.5	5.30	2.06
5	46.6	5.55	—
6	47.5	5.69	2.54
7	49.6	5.96	2.48
8	46.1	5.77	—
9	45.0	5.37	—
10	45.7	5.40	1.91
11	45.8	5.59	2.06
12	47.0	5.56	1.92

The optimum conditions for acetic acid were those of Test 7, the yield representing an increase of 30 per cent over that obtained without the use of steam; for naphtha the best yield is that for Test 6, representing an increase of 51 per cent.

As may be seen from the above table, with increase in the temperature of the steam there is a steady rise in the yield of acid up to a maximum and then a sharp decrease. At higher temperatures the yield rises again and then becomes more or less constant. Similar results were obtained with other materials, the figures when plotted giving the same type of curve.

For naphtha the figures show less regularity, probably owing to the fact that the methods of analysis are less exact and the risks of loss during the process are greater. In the above trials the naphtha carried away with the non-condensable gases was not recovered and determined.

The yield of charcoal is high, but in each test the material appeared to be fully carbonised. It will be noted that the figures do not vary greatly from the mean and the use of steam under these conditions would therefore appear to have practically no effect on the yield of the product.

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